

ANALYSIS OF BLOOD, HAIR, URINE, AND DUST SAMPLES  
FOR HEAVY METALS

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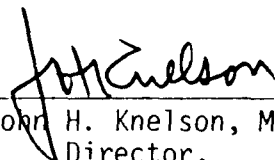
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## FOREWORD

The many benefits of our modern, developing, industrial society are accompanied by certain hazards. Careful assessment of the relative risk of existing and new man-made environmental hazards is necessary for the establishment of sound regulatory policy. These regulations serve to enhance the quality of our environment in order to promote the public health and welfare and the productive capacity of our Nation's population.

The Health Effects Research Laboratory, Research Triangle Park conducts a coordinated environmental health research program in toxicology, epidemiology, and clinical studies using human volunteer subjects. These studies address problems in air pollution, non-ionizing radiation, environmental carcinogenesis and the toxicology of pesticides as well as other chemical pollutants. The Laboratory develops and revises air quality criteria documents on pollutants for which national ambient air quality standards exist or are proposed, provides the data for registration of new pesticides or proposed suspension of those already in use, conducts research on hazardous and toxic materials, and is preparing the health basis for non-ionizing radiation standards. Direct support to the regulatory function of the Agency is provided in the form of expert testimony and preparation of affidavits as well as expert advice to the Administrator to assure the adequacy of health care and surveillance of persons having suffered imminent and substantial endangerment of their health.

The chemical analyses provided under this contract support a collaborative survey by the Center for Disease Control and the Environmental Protection Agency to assess metal absorption in children living in the vicinity of primary non-ferrous smelters. The results of the overall survey will be reported separately.

  
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## ABSTRACT

Communities from ten states in the United States and two cities in Mexico were studied. The communities were chosen for their proximity to primary non-ferrous smelter industries.

Three lead and five zinc smelter areas were sampled for blood, hair, and dust. Urine, blood, hair, and dust were collected from fourteen copper smelter sites and four control cities.

Samples were analyzed for arsenic, lead, cadmium, copper and zinc.

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## I. INTRODUCTION

Documentation of excessive absorption of heavy metals by children living near nonferrous metal smelters in the U. S. A. and Canada activated a nationwide study to determine the distribution of several heavy metals around primary lead, zinc, and copper smelters. Pre-school children were selected as test subjects because signs of absorption of heavy metals are more likely to appear with them than with older children or adults. The purpose of this project was to analyze tissue and dust samples collected from test subjects living within a two mile radius of each smelter so that heavy metal absorption could be evaluated.

Control sites were selected to provide background reference data as to the existing level of these heavy metals in areas not associated with nonferrous smelters.

## II. SUMMARY

The study encompassed collections from ten states in the U. S. A. and two cities in Mexico. Tissue and dust samples from preschool children and their homes were differentiated for analysis in accord with the type smelter or control being evaluated.

Three lead and five zinc smelter areas were sampled for blood, hair, and dust. Urine, blood, hair, and dust were collected from fourteen copper smelter sites and four control cities.

All dust samples were analyzed for As, Pb, Cd, Cu, and Zn. Hair samples from lead and zinc smelter sites were analyzed for Cd and Pb; while copper smelter sites and control areas received As, Pb, and Cd determinations. Urine collections (copper smelter sites and control areas) were measured for specific gravity and As. Lead and FEP were analyzed in blood from all three smelter types. Additionally, Cd was included for lead smelter sites; Cd and Zn for zinc smelter sites; and Cu and Zn for copper smelter sites. Control bloods were tested for all five blood parameters.

Internal and external quality control programs were integrated with sample analyses. Accuracy and precision data derived from these programs are reported and analyzed in depth.

Analyses for each collection site were reported in progressive order in accord with a numeric field assignment for individual subjects from

each participating family. The laboratory analyst and date for each determination, including quality controls, was shown within this format.



### III. CONCLUSIONS

The quality of the analytical results produced during this study has been evaluated in terms of uncertainty measurements which represent at least 95 percent confidence interval based on measurement error and variability between samples. The detrimental effects contributed by the samples themselves were successfully overcome in all sample types except urine. Overall accuracy and precision, expressed as relative percent, for each sample category is as follows: dust,  $\pm 3\%$ , hair,  $\pm 5\%$ , blood,  $\pm 10\%$ , and urine,  $\pm 49\%$ .

#### IV. RECOMMENDATIONS

Based on the experience gained in the performance of this contract, the following recommendations are suggested for the improvement of future projects of a similar nature:

- A. Dust - The smear technique employed in the collection of the dust samples has two significant shortcomings.

A sample of this type does not lend itself to any standard analytical quality control program. Since the entire sample cannot be removed, blind sample splits and recovery studies cannot be conducted.

Data obtained can be reported only in terms of micrograms of acid soluble metal per towlette (or per sample). Since the actual amount of sample collected varied widely, the ability to express the data as micrograms of metal per gram of dust would have allowed for an exact comparison of analytical data between collection sites, rather than the relative comparison which results from the method employed.

From a collection standpoint, dust is, perhaps, the most difficult sample type addressed in this project. Paint and other materials heavily laden with metals may be preferentially dissolved by the organic liquids in the towlettes. The abrasive nature of the sampling procedure contributes to the incorporation of these con-

taminants in the samples, and there is no procedure for obtaining an initial weight of the dust as it is collected.

A recommended dust collection technique, which the contractor has used, involves dusting a surface of sufficient size to render a sample adequate for complete analysis. A small camel's hair brush is used to sweep the sample into a small whirlpak. This disallows external contamination from the hands of field personnel, surface finishes, and/or the implement used for collection. The brush must, however, be thoroughly cleaned after each use.

- B. Urine - In order to combat the tendency for urine samples to preferentially precipitate with time lapse and temperature variations, a change in the collection protocol would be necessary.

Specific gravity measurements should be performed in the field as each sample is collected.

Since time lapse and temperature variations occur during storage and transport to the laboratory, urine samples should be shaken and aliquoted in the field as soon after collection as possible. If blind splits are to be made, this should also be performed at that time. This procedure would allow for homogeneity of each sample, and it would assure uniform analytical handling.

- C. Blood - Since clotted blood does not lend itself to uniform sample aliquoting techniques, two avenues are open as approaches to preclusion of this problem. First, sample splits could easily be made from the syringe while the blood is fresh and not clotted.

Secondly, a more uniform mixing with an anticoagulant could be applied. The former would, at this time, appear to be the safest and simplest.

All blood samples should be ejected from the syringe into containers appropriate for shipment. Inverted, leaky syringes held together with various types of tape do not constitute proper shipping vessels.

- D. Hair - The extreme variation of metals content in hair indicates that small samples are not representative of the overall hair of the subject. Thus, a concerted effort should be made to collect as large a sample as possible from each subject.

Zip-loc bags provide excellent transport containers; however, they should be locked carefully as soon as they receive a sample of hair. A secure seal allows for transport in a condition isolated from external contamination. Each hair sample should be handled with gloves and completely enclosed within the plastic bag.

Human scalp hair is widely used for assessing environmental exposure to metals. Trace metal content of hair is, likewise, reported to be an indicator of deficiency conditions in both humans and test animals. Because of these considerations and because of the ready availability of hair as a biopsy tissue, scalp hair lends itself well to environmental monitoring of humans for trace metal exposure.

A number of problems are apparent which could have significant influence on the interpretation of data for hair as a valid

biological indicator for environmental exposure. Findings from a series of pilot research studies conducted by the contractor, as in-house satellite investigations, clearly indicate the need to conduct a more closely controlled investigation in the area of trace metal analysis of hair. There is, thus, a need for the design of an analytical study to define, investigate, and establish the parameters which can adversely influence the interpretation of hair data.

The recommended research should study, for a period of at least two years, the trace metal content of scalp hair samples collected under carefully controlled conditions from a healthy population living in an area free from major point source atmospheric metal contamination. All pertinent background information relating to the sampling population should be made available so that relationships between trace metal contents and personal covariants can be evaluated. This requires an extensive, well-administered questionnaire. Participation in the program should be limited to those subjects who are willing and cooperate fully in providing all pertinent background information to be included in the study; therefore, the selection of the sampling population should be carefully controlled to assure that all vital areas are included in the study.

Since factors other than environmental exposure can play a significant role in trace metal concentrations and distributions, the study should address itself to the following potential factors:

- (1) Seasonal variations--i.e., hair growth rate and frequency of hair care.
- (2) Hair care--i.e., types and frequency of use of chemical products and their contribution to elemental alteration of hair.
- (3) Inherent variabilities--i.e., physical and physiological hair characteristics and metals content along single strands of hair.
- (4) Time effects--i.e., storage time for washed versus unwashed hair prior to analysis.
- (5) Participant characteristics--i.e., race, medical treatment, residence location, smoking habits, diet, sex, age, etc.

E. General Sampling Protocol - Consistency in adherence to a sampling protocol at each collection site is essential from a quality control standpoint. Certain basic guidelines should be followed in order to obtain data which can be compared directly and correlated with known varying parameters. These parameters should have been primarily limited to 1) geography, baseline conditions, and environmental exposure characteristics and 2) inherent biological uptake of heavy metals.

In order to produce data which represent a real profile of these conditions, one should properly and legibly code and permanently

label each sample as it is collected. Each individual sample should be treated precisely the same as all other samples of that particular type. The protocol should be realistic in terms of maximum time required to perform each field procedure. For example, frozen samples shipped over long distances should arrive, at the laboratory, in the same condition as those shipped from proximal collection sites.

Provided the recommended protocols for field sample procedures, as discussed for each sample type, are followed, all collections could be shipped directly to participating laboratories on an individual basis. This would eliminate variables such as time differentials, thawing of samples, inhomogenous aliquots, and misplacement of partial batches.

Also, uniformity of sample sizes submitted for analysis should be held at a reasonable tolerance level. All containers to be used in a project of this type should be procured from single line suppliers and, preferably, from a given manufacturing batch or lot.

Shipment schedules for submission of samples for analysis should be planned in advance and modes of transport carefully investigated.

A continuous rapport and conscientious use of quality control among persons responsible for field sampling, laboratory analyses, and project management are imperative in the obtainment of valid and useful analytical data.

## V. DISCUSSION OF ANALYTICAL APPROACH AND RESULTS

A. Preliminary Treatment for Sample Preparation - This project included receipt of human tissue and house dust from twenty-four sampling sites. Of these sites, three were near lead smelters, five near zinc smelters, twelve near copper smelters, and four were from control areas (Table 1). Because of deviations from the prescribed sampling protocol, a laboratory screening of those samples not meeting the minimum requirements for analysis was established. The criteria on which samples were rejected are shown in Table 2. The acceptable size limits were prescribed in the contract; however, additional measurements were required in the laboratory in order to differentiate samples which were very near the limit and could not be visually determined. The various procedures for handling these samples will be discussed on an individual basis for each sample type, and the rejections made for each collection site will be enumerated and related to their cause.

1. Procedures for Sample Screening--Each shipment contained samples from several collection sites and, therefore, required a preliminary sorting and assignment to an organized sequence for analysis. Once this process had been achieved, each sample type was individually screened for analytical acceptability.

a. Blood--The tubes were checked for cracks and/or probable contamination, and notations were recorded when appropriate. All samples which were not whole blood or could not be



Table 1. Breakdown of Samples Received Versus Samples Analyzed per Collection Site

TYPE	SAMPLING AREA LOCATION	CODE	SAMPLE COLLECTIONS					
			BLOOD		HAIR		URINE	
			RECEIVED	ANALYZED	RECEIVED	ANALYZED	RECEIVED	ANALYZED
Lead	Herculaneum, MO	HK	102	91	112	76		87
Lead	Bixby, MO	BX	50	48	59	20		40
Lead	Glover, MO	GL	35	23	37	30		31
Zinc	Bartlesville, OK	BV	90	87	95	80		65
Zinc	Corpus Christi, TX	CC	51	13	73	38		46*
Zinc	Monaca, PA	MN	65	63	78	65		0
Zinc	Palmerton, PA	PL	112	112	107	74		78
Zinc	Amarillo, TX	AM	97	95	92	40		52
Copper	Hayden, AZ	HA	99	99	109	105	92	69
Copper	Miami, AZ	MI	101	101	95	78	81	72
Copper	Morenci, AZ	MO	102	100	106	98	102	74
Copper	Ajo, AZ	AJ	107	107	101	86	78	69
Copper	Anaconda, MT	AN	70	65	87	87	75	57
Copper	McGill, NV	MC	52	51	64	47	53	45
Copper	San Manuel, AZ	SM	103	101	111	14	87	79
Copper	White Pines, MI	WP	72	71	86	81	68	84
Copper	Copper Hill, TN	CH	89	87	96	92	84	72
Copper	Douglas, AZ	DO	97	97	101	95	93	63
Copper	Aqua Prieta, Mexico	AP	99	98	105	74	88	54
Copper	Hurley, NM	HL	51	49	95	94	76	74
Control	Safford, AZ	SA	97	93	109	53	97	75
Control	Perryville, MO	PV	86	86	102	86	99	76
Control	Albuquerque, NM	AL	85	83	101	23	73	78
Control	Nogales, Mexico	NG	106	106	114	67	104	79

\* taken on cotton balls

TABLE 2. Criteria for Rejection of Samples  
from the Project.

<u>Sample Tissue Type</u>	<u>Criteria for Rejection</u>
Blood	< 1 ml not complete whole blood indeterminant code identification
Hair	< 0.2 gm indeterminant code identification
Urine	< 25 ml indeterminant code identification samples not contracted
Dust	taken on materials other than towelettes indeterminant code identification

identified from labels were counted and discarded.

After thawing, the blood volumes were individually compared visually against a reference 1 ml blood sample. Those samples determined to be <1 ml were counted and discarded; however, because of excessive clotting and the large number of samples which were close to the 1 ml volume, some samples were processed and analyzed for FEP and later discarded for further analysis. This was done after the blood was transferred to a graduated cylinder for volumetric measurement. FEP determinations were made prior to this transfer because of the prescribed time requirement in the method. All blood samples which had been rejected were reassembled and enumeration checks were finalized.

- b. Hair--Since hair and dust were frequently shipped in bags together, a separation and verification of code assignments of these samples was necessary prior to screening. Samples obviously too small and/or with unidentifiable labels were rejected. Improperly sealed bags were noted as were containers other than Zip-locs. A second screening of hair was attempted by weighing borderline samples on a top loading balance. If the weights were between 0.20 and 0.25 gm, the samples were reentered and coded for analysis. Some of these samples fell below the 0.2 gm limit when reweighed on an analytical balance after they had been cleaned and dried. These final discards were added to all of the hair previously rejected, and proper notations were recorded.

c. Urine--Some shipments contained urine from lead and zinc smelter sites, which were not to be included for analysis under this contract; therefore, these samples were rejected. Each of the samples included for analysis was compared, after thawing, to a reference urine of a 25 ml volume. All samples failing to meet this criterion were enumerated and rejected.

d. Dust--After separation from hair samples (see Hair above), dust was observed for adherence to sampling protocols and analytical preferences. Since only ten samples per collection site were to be chosen, properly sealed bags with no evidence of contamination received top consideration. Apparent sample size and legibility of label codes were then utilized as secondary criteria. One entire shipment of dust from Corpus Christi, Texas, was discarded because the samples had been taken on cotton balls and blanks were unavailable. Rejected dust samples were enumerated after all these selection criteria had been imposed.

2. Sample Conditions and Handling Techniques--The sample conditions and the various procedures for handling these samples are presented on an individual basis for each sample type according to collection site. A summary of samples received versus samples analyzed is given in Table 1.

a. Lead Smelters--The lead smelter samples were to be analyzed for: FEP, Pb, and Cd in blood; Pb and Cd in hair; and Pb,

Cd, Zn, Cu, and As in dust. Of the 187 bloods received, 162 were completely analyzed; of the 208 hair samples, 126 were completely analyzed; and of the 158 dust samples, the prescribed 30 were appropriate for complete analysis. The following is a resume of the condition of sample shipments and preliminary analytical treatment of samples received from each lead smelter.

HERCULANEUM, MO

General - Samples received 9/18/75 with no instructions  
therefore all samples initially coded

Blood - All thawed; 28 badly clotted therefore duplicate  
FEP's run; condition required special mixing for  
Cd; 11 run for FEP only

Hair - Zip-locs sealed; 36 rejects

Urine - Received 108 not to be analyzed--all were coded

Dust - Zip-locs not sealed; 77 screened

BIXBY, MO

General - Samples received 9/25/75

Blood - Partially thawed; 2 badly clotted therefore  
duplicate FEP's run; condition required special  
mixing for Cd

Hair - Zip-locs and sealed; 39 rejects

Urine - Samples received but not to be analyzed

Dust - Zip-locs and sealed; 30 screened

GLOVER, MO

General - Samples received 9/25/75

Blood - Partially thawed; 1 badly clotted therefore  
duplicate FEP run; condition required special  
mixing for Cd

Hair - Zip-locs and sealed; 7 rejects

Urine - Samples received but not to be analyzed

Dust - Zip-locs and sealed; 21 screened



- b. Zinc Smelters - The zinc smelter samples were to be analyzed for FEP, Pb, Cd, and Zn in blood; Pb and Cd in hair; and Pb, Cd, Zn, Cu, and As in dust. Total analyses were completed for 370 of the 415 bloods received, 297 of the 445 hair samples, and 30 of the prescribed 50 from a total of 241 dust samples. A resume of each zinc smelter follows.

BARTLESVILLE, OK

General - Samples received 9/18/75 with no instructions  
therefore all samples initially coded

Blood - All thawed; all in inverted syringes; 13 with  
white adhesive tape, 59 with black electrical  
tape, 18 with scotch tape; 3 badly clotted  
therefore duplicate FEP's run; condition  
required special mixing for Cd; 3 for FEP only

Hair - Alligator sandwich bags with twist ties; 15 rejects

Urine - Received 75 not to be analyzed--all were coded

Dust - Alligator sandwich bags with twist ties, towelettes  
very dry; 55 screened

CORPUS CHRISTI, TX

General - Samples received 11/18/75 and 11/20/75; all samples had to be re-coded from information received from CDC

Blood - Partially or completely thawed; received 51 samples, 38 of which were rejects because they had been spun down and only plasma separates were shipped; condition required special mixing for Cd on the 13 whole blood samples

Hair - Zip-locs sealed; 35 rejects

Urine - Samples received but not to be analyzed

Dust - Zip-locs sealed but all 46 were rejects because they had been taken on cotton balls instead of towelettes

MONACA, PA

General - Samples received 11/18/75, 12/5/75, and 12/16/75

Blood - First and second shipments partially thawed--third shipment (4) not iced at all; 3l badly clotted therefore duplicate FEP's run; condition required special mixing for Cd; third shipment (4) received after coding, causing handling and data processing problems because of skips in numerical sequence

Hair - Zip-locs and sealed; 13 rejects

Urine - Samples received but not to be analyzed

Dust - No samples received

PALMERTON, PA

General - Samples received 1/9/76

Blood - Frozen; 2 badly clotted therefore duplicate  
FEP's run; condition required special mixing  
for Cd

Hair - Zip-locs sealed; 33 rejects

Urine - Samples received but not to be analyzed

Dust - Zip-locs sealed; 68 screened

AMARILLO, TX

General - Samples received 1/9/76

Blood - Frozen; 1 badly clotted therefore duplicate  
FEP run; condition required special mixing for  
Cd

Hair - Zip-locs mostly sealed; 52 rejects

Urine - Samples received but not to be analyzed

Dust - Zip-locs mostly sealed; 42 screened

c. Copper Smelters - The copper smelter samples were to be analyzed for: FEP, Pb, Zn, and Cu in blood; Pb, Cd, and As in hair; specific gravity and As in urine; and Pb, Cd, Zn, Cu, and As in dust. Of the 1046 bloods received, 1026 were completely analyzed; of the 1156 hair samples, 951 were analyzed; of the 977 urines, 793 were analyzed; and of the 812 dust, the prescribed 120 were appropriate for complete analysis. A resume of each copper smelter follows.

HAYDEN, AZ

General - Samples received 9/18/75 with no instructions  
therefore all samples initially coded; all samples  
completely mixed with MI

Blood - Partially thawed; labels extremely difficult  
to read; 12 badly clotted therefore duplicate  
FEP's run

Hair - Zip-locs mostly not sealed; 4 rejects

Urine - Partially thawed; 8 rejects; precipitated

Dust - Zip-locs mostly not sealed; 59 screened



MIAMI, AZ

General - Samples received 9/18/75 with no instructions  
therefore all samples initially coded; all samples  
completely mixed with HA

Blood - Partially thawed; labels difficult to read; 18  
badly clotted therefore duplicate FEP's run

Hair - Zip-locs mostly not sealed; 17 rejects

Urine - Partially thawed; 9 rejects; precipitated

Dust - Zip-locs mostly not sealed; 62 screened

MORENCI, AZ

General - Samples received 9/25/75

Blood - Partially thawed; 7 badly clotted therefore  
duplicate FEP's run

Hair - Zip-locs sealed; 8 rejects

Urine - Completely thawed; 25 rejects; heavily precipitated

Dust - Zip-locs sealed; 64 screened

AJO, AZ

General - Samples received 10/15/75 and 10/30/75

Blood - Partially thawed; 8 badly clotted therefore  
duplicate FEP's run

Hair - Zip-locs sealed; 15 rejects

Urine - Partially thawed; 9 rejects; precipitated; 6  
samples received too late to run with scheduled  
batch

Dust - Zip-locs sealed; 59 screened

ANACONDA, MT

General - Samples received 10/30/75

Blood - Thawed; 3 badly clotted therefore duplicate  
FEP's run

Hair - Zip-locs mostly sealed

Urine - Partially thawed; 33 rejects; precipitated

Dust - Zip-locs mostly sealed; 47 screened

McGILL, NV

General - Samples received 10/30/75

Blood - Thawed; 4 badly clotted therefore duplicate  
FEP's run

Hair - Zip-locs mostly sealed; 17 rejects

Urine - Partially thawed; bad leakage in shipping  
container; 4 rejects; precipitated

Dust - Zip-locs mostly sealed; 35 screened

SAN MANUEL, AZ

General - Samples received 10/30/75

Blood - Thawed; 14 badly clotted therefore duplicate  
FEP's run; 29 samples sent in inverted syringes,  
untaped; tubes cracked and bad leakage on samples  
and container; codes very difficult to read

Hair - Zip-locs mostly sealed; 97 rejects

Urine - Thawed; slight leakage in container; 32 rejects;  
heavily precipitated

Dust - Zip-locs mostly sealed; 69 screened

WHITE PINES, MI

General - Samples received 11/18/75

Blood - Partially thawed; 1 badly clotted therefore  
duplicate FEP run; 1 FEP only

Hair - Zip-locs partially sealed or not sealed; bags  
contaminated with blood; 5 rejects

Urine - Partially thawed; codes very difficult to read;  
9 rejects; precipitated

Dust - Zip-locs partially sealed or not sealed; bags  
contaminated with blood; 74 screened

COPPER HILL, TN

General - Samples received 11/18/75, 11/20/75, and 12/16/75

Blood - Partially or completely thawed; 12 badly clotted  
therefore duplicate FEP's run

Hair - Zip-locs sealed; 4 rejects

Urine - Partially or completely thawed; some codes very  
difficult to read; 19 rejects; heavily precipitated;  
15 samples received too late to run with scheduled  
batch

Dust - Zip-locs sealed; 62 screened



DOUGLAS, AZ

General - Samples received 11/18/75 and 11/20/75

Blood - Partially thawed; 7 badly clotted therefore  
duplicate FEP's run

Hair - Zip-locs sealed; 6 rejects

Urine - Partially thawed; 13 rejects; precipitated

Dust - Zip-locs sealed; 53 screened

AQUA PRIETA, MEXICO

General - Samples received 11/18/75 and 11/20/75

Blood - Partially or completely thawed; 11 badly clotted  
therefore duplicate FEP's run

Hair - Zip-locs partially sealed or not sealed; 31  
rejects

Urine - Partially or completely thawed; 13 rejects;  
heavily precipitated

Dust - Zip-locs partially sealed or not sealed; 44 screened

HURLEY, NM

General - Samples received 1/9/76

Blood - Frozen

Hair - Zip-locs sealed; 1 reject

Urine - Frozen; codes very difficult to read; 19 rejects;  
precipitated

Dust - Zip-locs sealed; 64 screened

d. Control Areas - The control samples were to be analyzed for: FEP, Pb, Cd, Zn, and Cu in blood; Pb, Cd, and As in hair; specific gravity and As in urine; and Pb, Cd, Zn, Cu, and As in dust. Complete analyses were achieved on 368 of the 374 bloods, 229 of the 426 hair samples, 291 of the 373 urines, and the 40 prescribed dust samples from a total of 308. The following is a resume of each control area:

SAFFORD, AZ

General - Samples received 12/5/75 and 12/16/75

Blood - First shipment frozen or partially thawed; second shipment (10) not iced at all; 11 badly clotted therefore duplicate FEP's run; condition required special mixing for Cd; second shipment (10) received after coding, causing handling and data processing problems because of skips in numerical sequence

Hair - Zip-locs sealed; 56 rejects

Urine - Partially thawed; 35 rejects; precipitated

Dust - Zip-locs sealed; 65 screened

PERRYVILLE, MO

General - Samples received 12/5/75 and 12/16/75

Blood - First shipment frozen or partially thawed; second shipment (9) not iced at all; 5 badly clotted therefore duplicate FEP's run; conditions required special mixing for Cd; second shipment (9) received after coding, causing handling and data processing problems because of skips in numerical sequence

Hair - Zip-locs sealed; 16 rejects

Urine - Partially thawed; 18 rejects; precipitated

Dust - Zip-locs sealed; 66 screened

ALBUQUERQUE, NM

General - Samples received 12/5/75 and 12/16/75; all samples not properly labeled--lacked child code, sent coding sheets to CDC for corrections

Blood - First shipment frozen or partially thawed; second shipment (9) not iced at all; 7 badly clotted therefore duplicate FEP's run; condition required special mixing for Cd; second shipment (9) received after coding, causing handling and data processing problems because of skips in numerical sequence

Hair - Zip-locs not sealed; 78 rejects

Urine - Thawed; 22 rejects; heavily precipitated

Dust - Zip-locs not sealed; 68 screened

NOGALES, MEXICO

General - Samples received 12/5/75

Blood - Frozen; 15 badly clotted therefore duplicate

FEP's run; condition required special mixing for

Cd

Hair - Zip-locs mostly sealed; 47 rejects

Urine - Frozen; 7 rejects; precipitated

Dust - Zip-locs mostly sealed; 69 screened



B. Special Research Studies - The deviations of the actual samples received from the Government specification as set forth in the RFP were of such magnitude that it was necessary to conduct two special research studies before a final analysis scheme could be established.

1. Urine Precipitate Problems--Essentially, all urine samples contained a precipitate. Since a number of arsenic compounds are extremely volatile, heating the sample to dissolve the precipitate was not a feasible approach. The best solution to the problem would have been to prepare the entire sample, as received, for analysis. However, this solution to the problem was not economically feasible. The extreme variability in sample size would have required custom adjustments of the amount of digestion acid required for dissolution, as well as the final sample volume. These adjustments would, therefore, create preparation procedures unique for each individual urine sample. Additionally, data retrieval, key-punching, and verification involvement would have increased by more than a factor of three.

The only practical approach to the problem was to try to remove a representative aliquot from each sample. One of the larger urine samples from a lead smelter area was shaken vigorously and divided into four aliquots of 25 ml each and one final sample of 19 ml. All were analyzed for arsenic.

Results: As =  $34 \text{ ppb} \pm 6 \text{ ppb}$  (or  $3.4 \pm 0.6 \text{ } \mu\text{g}/100 \text{ ml}$ )  
(95% Confidence Interval)

Coefficient of Variation = 8.82%

Based on these data, this aliquoting approach was adopted as a compromise preparation procedure. Actual experience with the samples in the contract revealed that some samples produced a relatively homogeneous sample after vigorous shaking while others still contained rather large precipitated aggregates.

2. Dust Collection Background Study--The RFP specifications called for dust samples of at least 100 mg. In actuality, the dust samples were collected by a technique<sup>1</sup> which does not allow for an actual measurement of the weight of the dust collected. A dust smear was collected from the top of a door facing using a moist, disposable paper towel, size 14 X 20 cm (44 in<sup>2</sup>) impregnated with 20% denatured alcohol and 1:750 benzalkonium chloride. The towelette most frequently used was Wash 'n Dri from Canaan Products, Inc., Canaan, Conn. Because of the inconsistency in the manner by which the samples were taken and because of the varying mass of the dust collected, the only analysis avenue open was to employ the sample preparation procedure used by Vostal and associates in their study.

Actual blank towelettes from the lots used to sample the smelters were not available for background determinations. Consequently, background data were obtained from one box of 26 towelettes

<sup>1</sup> Vostal, J. Tares, E. Sayre, J. W., and Charney, E.,  
Environmental Health Perspectives, May, 1974, p 71.

supplied to the Contractor by CDC. The results obtained for the towelette background contribution are contained in Table 3. Appropriate background corrections were applied to all dust data. Data obtained by the above described method are representative of the 0.1 N HCL soluble content of the samples. No relationship can be established between this value and the total metal content of the dust.

C. Analytical Methodology and Discussion - A number of modifications in the analytical approach and methodology proposed by the Contractor for the fulfillment of this contract were required because of the size and condition of the samples actually received for analysis. This section discusses these modifications and the analytical methods actually employed.

1. FEP Analysis of Blood--The original RFP specified that blood samples would be maintained on ice in the dark from time of collection until an aliquot was taken for FEP determination at the contracting laboratory. Based on the assumption that the samples would be handled in the prescribed manner, the method chosen by the Contractor for the FEP determination was the method of Joselow which measures the fluorescence of zinc protoporphyrin. When the samples arrived, it was learned that many had been collected for three months or more and stored in a frozen state for varying periods of time. It was, therefore, necessary to change from the method of Joselow to the method of Sassa; and measure all erythrocyte porphyrins. The analytical

TABLE 3. Towelette Background Data

Concentrations are expressed as total micrograms per towelette

<u>Sample No.</u>	<u>Lead</u>	<u>Cadmium</u>	<u>Arsenic</u>	<u>Copper</u>	<u>Zinc</u>
R 3214	<0.25	<0.025	<0.025	1.75	3.25
R 3215	<0.25	<0.025	<0.025	1.25	3.00
R 3216	<0.25	<0.025	<0.025	1.63	4.50
R 3217	<0.25	<0.025	<0.025	1.81	1.00
R 3218	<0.25	<0.025	<0.025	1.88	4.25
R 3219	<0.25	<0.025	<0.025	1.40	4.13
R 3220	<0.25	<0.025	<0.025	1.50	11.8
R 3221	<0.25	<0.025	<0.025	1.38	3.50
R 3222	<0.25	<0.025	<0.025	1.63	4.75
R 3223	<0.25	<0.025	<0.025	1.88	3.25
Mean Value	<0.25	<0.025	<0.025	1.61	4.34

method of Sassa is the referee method employed by CDC for FEP determinations.<sup>2</sup>

2. Analysis of Blood for Heavy Metals--The original sample preparation proposed by the Contractor called for the samples to be lyophilized and for the organic matrix to be destroyed by oxygen-flask combustion. Prior to this step, however, a microsample (50  $\mu$ l) was to be removed for lead analysis by direct flameless atomic absorption spectroscopy. The presence of many macroclotted blood samples made it impossible to withdraw valid microsamples for the blood lead analyses. To overcome this problem, the proposed sample preparation scheme for blood was replaced with a wet, acid-oxidation preparation of the total sample (NIOSH Methods P & CAM 101 and 139).

The acid digest solution was then analyzed by conventional atomic absorption for copper and zinc and the lead was determined by direct flameless atomic absorption (using a graphite furnace with multi-linear temperature programming and simultaneous background correction).

At this time, a request was received from the Project Officer to add an analysis for cadmium on selected blood samples. Preliminary investigation revealed that the blank correction for the acid-digestion sample preparation was too high for cadmium to give reliable analytical data. The following analytical procedure was found to give acceptable results in all cases except for those with excessive macroclots. Blood samples, in

<sup>2</sup>Granick, S., Sassa, S., Granick, J. L., Levere, R. D., and Kappas, A. (1972) Proc. Nat. Acad. Sci. USA. 69, 9, 2381-2385.

their original collection containers, were placed on a vortex mixer for two minutes. A 250 µl sample was withdrawn with an Eppendorf pipette and diluted to five ml with distilled water. An equal aliquot of sample and 1% ammonium sulfate solution (Cd free) were placed in a pyrolytic graphite tube and analyzed by flameless atomic absorption.

3. Analysis of Hair for Heavy Metals--All hair samples were washed with agitation for 30 minutes in a non-ionic detergent (7-X-O-Matic) and thoroughly rinsed with distilled deionized water. Samples were then dried (vacuum oven 60° C, 0.5 atm.) and weighed. The original proposal called for the organic matrix to be destroyed by oxygen-flask combustion. This, however, was replaced with the acid-oxidation preparation technique being used for blood and urine since the results obtained by both techniques are comparable. Conventional atomic absorption was employed for the analysis of cadmium and lead in hair while the gaseous hydride atomic absorption method was used for arsenic.
4. Analysis of Urine for Arsenic--The method originally proposed and actually used for the analysis of arsenic in urine is the NIOSH Method No. P & CAM 139. The samples are ashed with a mixture of nitric, perchloric, and sulfuric acids to destroy the organic matrix. The ash is treated with ammonium oxalate to remove traces of nitric acid and the solution is analyzed by atomic absorption of the gaseous hydride (arsine).
5. Analysis of House Dust--The Contractor originally proposed to

follow the sample preparation procedure for house dust given in the RFP as the recommended method. Specifically, the "as received" sample was to be weighed and then sieved through a 0.5 mm screen while being shaken for five minutes at 260 oscillations per minute. The sieved portion was then to be weighed and extracted with quartz distilled nitric acid (6N) at 50° C for 30 minutes. The extract was then to be filtered and analyzed for Pb, Cd, Zn, and Cu by atomic absorption.

An aliquot of the filtered HNO<sub>3</sub> acid extract was to be treated to remove all traces of nitric acid and then analyzed for arsenic by the gaseous hydride-atomic absorption technique.

Additionally, on a selected number of house dust samples, an extract was to be made on a portion of the unsieved sample and a comparative analysis was to be made on both sieved and unsieved portions.

As stated in the previous section of this report, the dust samples were collected on moist, commercial towelettes. The sample preparation method prescribed for use in the RFP is applicable only to dust free from the collection matrix. Consequently, the entire sample, towelette plus dust, was soaked at room temperature for 16 hours in 20 ml of 0.1 N HCL. The eluates were decanted, final volume was adjusted to 25 ml, and analyses were performed for the elements of interest--conventional atomic absorption for Pb, Cd, Zn, Cu, and atomic absorption of a gaseous hydride for As.

In summary, the employed analytical methodology represents

current, state-of-the-art approaches which are basically sound from a technical standpoint. Documentation of the accuracy and precision of the methods are contained in the section of this report which deals with the internal analytical quality control program. The limits of detection for the various elements in the appropriate analysis solutions are contained in Table 4.

- D. Review of Quality Control Program - This contract required two quality control programs--a documented internal analytical quality control program, not to exceed 10% of the total effort, and an external control program, not to exceed 1%. All quality control efforts were in addition to the contract samples.

The internal quality control program encompassed blind split sample analyses for hair, blood, and urine; blind random analyses of standard reference samples; recovery and precision studies from two large, composite samples (blood and hair); and the analysis of standard sample splits with two reference laboratories.

The external control program was to consist of blind split sample analyses, blind known samples to be analyzed concurrently with contract batches of samples, and duplicate determinations to be performed by reference laboratories.

Each 50th blood and urine sample was split into two parts by the Contractor and one of the aliquots of each was analyzed by the Contractor. The other portion was delivered to the EPA Project Officer for analysis in EPA's laboratory. The Contractor was not required to split hair samples for duplicate analysis as a part of the Scope of Work of the contract.



TABLE 4. Limits of Detection

Concentration units are micrograms per liter (parts per billion)

<u>Element</u>	<u>Detection Limit, ppb</u>
Arsenic	1.
Copper	10.
Zinc	10.
Lead	
Conventional A.A.	10.
Flameless A.A.	0.5
Cadmium	
Conventional A.A.	1.
Flameless A.A.	0.02

This section of the final report deals with the internal analytical quality control program. Because of the importance of laboratory analyses and the resulting actions which they produce, a program to insure the reliability of the data is essential. Data from a valid analytical quality control program provide an assessment and measurement of the precision and accuracy of the analytical results. In addition, a properly designed and conducted program will identify any segment of the total effort which is "out of control."

1. Accuracy--Accuracy refers to the degree of difference between observed and known, or actual values. Two approaches were used to establish the accuracy of the analytical data--recovery studies and the analysis of standard reference materials.
  - a. Recovery Studies--These studies were conducted on an actual sample and not on reference standards. At the outset of this project, a pint of blood was secured from the local blood bank. The entire sample was lyophilized and homogenized to form a large, stable blood composite for use in the internal quality control program. Known amounts of copper, zinc, and lead were added to an aliquot of the control blood sample. Using the composite lyophilized blood sample, with known concentrations of 17.5 µg/g zinc, 4.60 µg/g copper, and 0.79 µg/g lead, recoveries were 98%, 99%, and 97% respectively. Individual results of this study are found in Table 5.
  - b. Standard Reference Materials (SRM) Analysis--Two standard samples were used to provide a measure of the control of accuracy

TABLE 5. Recovery Study Data

Concentration units are micrograms per gram lyophilized whole blood

Copper

<u>Sample No.</u>	<u>Sample Concentration</u>	<u>Added Spike</u>	<u>Sample Plus Spike</u>	<u>Percent Recovery</u>
R 3007	4.60	3.0	7.78	102.
R 3008	4.60	3.0	7.35	97.
R 3009	4.60	3.0	7.65	101.
R 3010	4.60	3.0	7.45	98.
R 3011	4.60	3.0	7.36	97.
Average Recovery				99.%

Zinc

<u>Sample No.</u>	<u>Sample Concentration</u>	<u>Added Spike</u>	<u>Sample Plus Spike</u>	<u>Percent Recovery</u>
R 3012	17.5	10.0	26.1	95.
R 3013	17.5	10.0	27.0	97.
R 3014	17.5	10.0	28.3	103.
R 3015	17.5	10.0	25.4	92.
R 3016	17.5	10.0	28.0	103.
Average Recovery				98.%

Lead

<u>Sample No.</u>	<u>Sample Concentration</u>	<u>Added Spike</u>	<u>Sample Plus Spike</u>	<u>Percent Recovery</u>
R 3017	0.79	1.0	1.68	94.
R 3018	0.79	1.0	1.88	105.
R 3019	0.79	1.0	1.70	95.
R 3020	0.79	1.0	1.64	92.
R 3021	0.79	1.0	1.73	97.
Average Recovery				97.%

during the analysis stage of the contract. These two samples were Lyophilized Bovine Liver (SRM 1577) from the National Bureau of Standards and Dried Animal Whole Blood (Code No. A-2/1974) from the International Atomic Energy Commission.

Prior to the analysis of any samples from the contract, eight aliquots from each of these reference materials were prepared for analysis in order to verify the proposed analytical methodology.

The bovine liver sample was analyzed first. Results of these tests are contained in Table 6 . These data show no significant difference between the actual analysis mean and the certified value for cadmium, lead, and zinc. However, a relative error of +3.59% was observed in the case of copper. Subsequent investigation traced the bias to the master copper standard employed for the atomic absorption analysis. This problem was corrected, and the animal blood standard samples were analyzed. Results for these samples are found in Table 7. All of the elements analyzed, including copper, showed no significant difference between the actual analysis mean and the recommended values for the standard.

In order to provide a measure of accuracy from analysis batch to batch, a blind sample of one of these standard reference samples was analyzed with the samples from each

TABLE 6. Analysis of Standard Reference Material 1577 Bovine Liver

Source: National Bureau of Standards

Concentrations are expressed as micrograms per gram (ppm)

<u>Sample No.</u>	<u>Copper</u>	<u>Zinc</u>	<u>Lead</u>	<u>Cadmium</u>
R 3030	199.	137.	0.33	0.27
R 3031	209.	135.	0.25	0.31
R 3032	201.	131.	0.31	0.28
R 3033	204.	128.	0.35	0.25
R 3034	192.	128.	0.35	0.26
R 3035	188.	133.	0.36	0.29
R 3036	186.	130.	0.36	0.27
R 3037	197.	138.	0.36	0.26
Mean Value (95% Confidence Interval)	197. $\pm$ 6.6	133. $\pm$ 3.3	0.33 $\pm$ 0.03	0.27 $\pm$ 0.02
Coefficient of Variation	4.02%	2.93%	11.4%	7.02%
Standard Values (95% Confidence Interval)	193. $\pm$ 10	130. $\pm$ 10	0.34 $\pm$ 0.08	0.27 $\pm$ 0.04

TABLE 7. Analysis of Dried Animal Whole Blood, Reference Material  
(Code No. A-2/1974)

Source: International Atomic Energy Commission

Concentrations are expressed as micrograms per gram (ppm)

<u>Sample No.</u>	<u>Copper</u>	<u>Zinc</u>	<u>Lead</u>
R 3022	50.5	88.6	0.86
R 3023	51.6	90.2	0.89
R 3024	44.3	89.4	0.99
R 3025	45.0	86.7	0.90
R 3026	51.5	88.4	0.96
R 3027	47.2	90.3	0.90
R 3028	44.1	91.2	0.97
R 3029	43.9	88.7	0.96
Mean Value (95% Confidence Interval)	47.3 $\pm$ 2.9	89.2 $\pm$ 1.2	0.93 $\pm$ 0.04
Coefficient of Variation	7.26%	1.57%	5.03%
Standard Values (95% Confidence Interval)	45. $\pm$ 6	89. $\pm$ 9	0.97 $\pm$ 0.22

smelter and/or control site. These data are tabulated in Tables 8 and 9. An examination of these data shows no significant deviation from the standard value of the reference samples.

Based on both the recovery studies and the actual analysis of these standard reference materials, it can be stated that at the 95% confidence interval the overall accuracy of the analytical data is 98% or better.

2. Precision--Precision is a measure of mutual agreement among individual measurements of the same property under prescribed similar conditions. In an analytical quality control program, precision is determined, not on reference standards, but by the use of actual samples which incorporate the inherent matrix variables associated with the sample type under investigation.
  - a. Quality Control Charts--Analytical quality control charts visibly represent the continuing validity of routine analytical data and the performance of individual analysts within a given laboratory. Limits for these control charts are calculated using the repeatability standard deviation for the control sample. Upper and lower control limits (UCL and LCL) are defined as  $\pm 3$  standard deviations while upper and lower warning limits (UWL and LWL) are set at  $\pm 2$  standard deviations. For any given period, if all points on the control chart are within the control limits and somewhat randomly distributed about the mean value, it can be

TABLE 8. Analysis of IAIA Animal Blood (Code No. A-2/1974)

<u>Sample No.</u>	<u>Batch No.</u>	<u>Copper</u>	<u>Zinc</u>	<u>Lead</u>
GF 6129	2	50.5	89.0	0.86
GF 6131	2	46.1	94.5	0.96
GF 5079	3	44.4	86.3	0.89
GF 5080	3	42.8	85.2	0.90
GF 5861	4	47.9	88.6	0.99
GF 6040	4	51.2	89.0	0.97
GF 6240	5	48.7	91.8	0.90
GF 6385	5	42.3	93.4	0.96
GF 7164	6	44.6	82.9	0.93
GF 7363	6	43.0	85.6	0.99
Mean Value (95% Confidence Interval)		46.2 $\pm$ 2.3	88.6 $\pm$ 2.7	0.94 $\pm$ 0.03
Coefficient of Variation		7.06%	4.23%	4.87%
Standard Values (95% Confidence Interval)		45. $\pm$ 6	89. $\pm$ 9	0.97 $\pm$ 0.22



TABLE 9. Analysis of NBS Bovine Liver (SRM 1577)

<u>Sample No.</u>	<u>Batch No.</u>	<u>Copper</u>	<u>Zinc</u>	<u>Lead</u>
GF 5582	2	201.	135.	0.33
GF 5583	2	194.	128.	0.35
GF 5824	3	190.	133.	0.25
GF 5893	3	194.	130.	0.36
GF 5811	4	189.	136.	0.31
GF 5938	4	193.	128.	0.36
GF 6217	5	195.	128.	0.35
GF 6359	5	201.	130.	0.36
GF 7072	6	203.	126.	0.30
GF 7310	6	189.	134.	0.39
GF 7473	6	194.	131.	0.40
Mean Value (95% Confidence Interval)		195. $\pm$ 3.3	131. $\pm$ 2.2	0.34 $\pm$ 0.03
Coefficient of Variation		2.51%	2.51%	12.5%
Certified Values (95% Confidence Interval)		193. $\pm$ 10	130. $\pm$ 10	0.34 $\pm$ 0.08

assumed that the precision of the analyses is consistent with the precision of the internal quality control sample.

The quality control sample used to generate the quality control charts relating to blood analyses was an aliquot of the lyophilized blood composite used for the recovery study. A fresh urine composite sample was used for the arsenic control. Representative quality control charts generated through the use of these samples are illustrated by Figures 1-10. Typical variability in precision among analysts is demonstrated by a comparison of Figures 1-3 and 4-6. These charts profile the precision of the analytical methodology employed for the analysis of lead, zinc, and copper in blood and arsenic in urine. Comparable charts were also developed for the analysis of arsenic, lead, and cadmium in hair and cadmium in blood.

A summary of the statistical profile generated by the control chart data is contained in Table 10. The following measures apply:

Standard Deviation (s). The square root of the variance.

$$s = \sqrt{\frac{\sum_{i=1}^n (x_i - \bar{x})^2}{n-1}}$$

where  $\bar{x}$  is the mean of the samples.

Coefficient of Variation (V) or Percent  
Relative Standard Deviation (% RSD).

$$V = \frac{100 s}{\bar{x}}, \quad \text{where } \bar{x} \text{ is the mean and } s \text{ the standard deviation of the sample.}$$

95% Confidence Interval. The interval expressed by

$\bar{x} \pm t(v, F=.975)s/\sqrt{n}$ , where  $v = n-1$  and where  $t$  is taken from tables of the t-distribution, is sufficiently wide to grant that the mean of the whole population has a 95% chance of falling in the interval. Such tables may be found in most of the CRC mathematics publications.

The average coefficient of variation for the four elements is 3.91%. The range exhibited by V is 1.15% to 5.98%.

- b. Composite Hair Analysis--Two composite hair samples were a part of the internal quality control program. In order to establish the inherent variability of a given hair sample, a special study was designed using one of these composites. The entire sample (~ 10 grams) was washed and dried according to routine standard procedures. The sample was then cut into one-quarter inch lengths and mixed thoroughly. Ten aliquots of the dried hair, weighing 0.5 gm each, were removed and analyzed individually. The remainder of the hair was initially processed as one sample; then, after dissolution, ten aliquots were removed from the prepared sample solution and analyzed.

FIGURE 1. CONTROL CHART FOR ZINC IN BLOOD ANALYST: 17  
DATE: 12-11-75

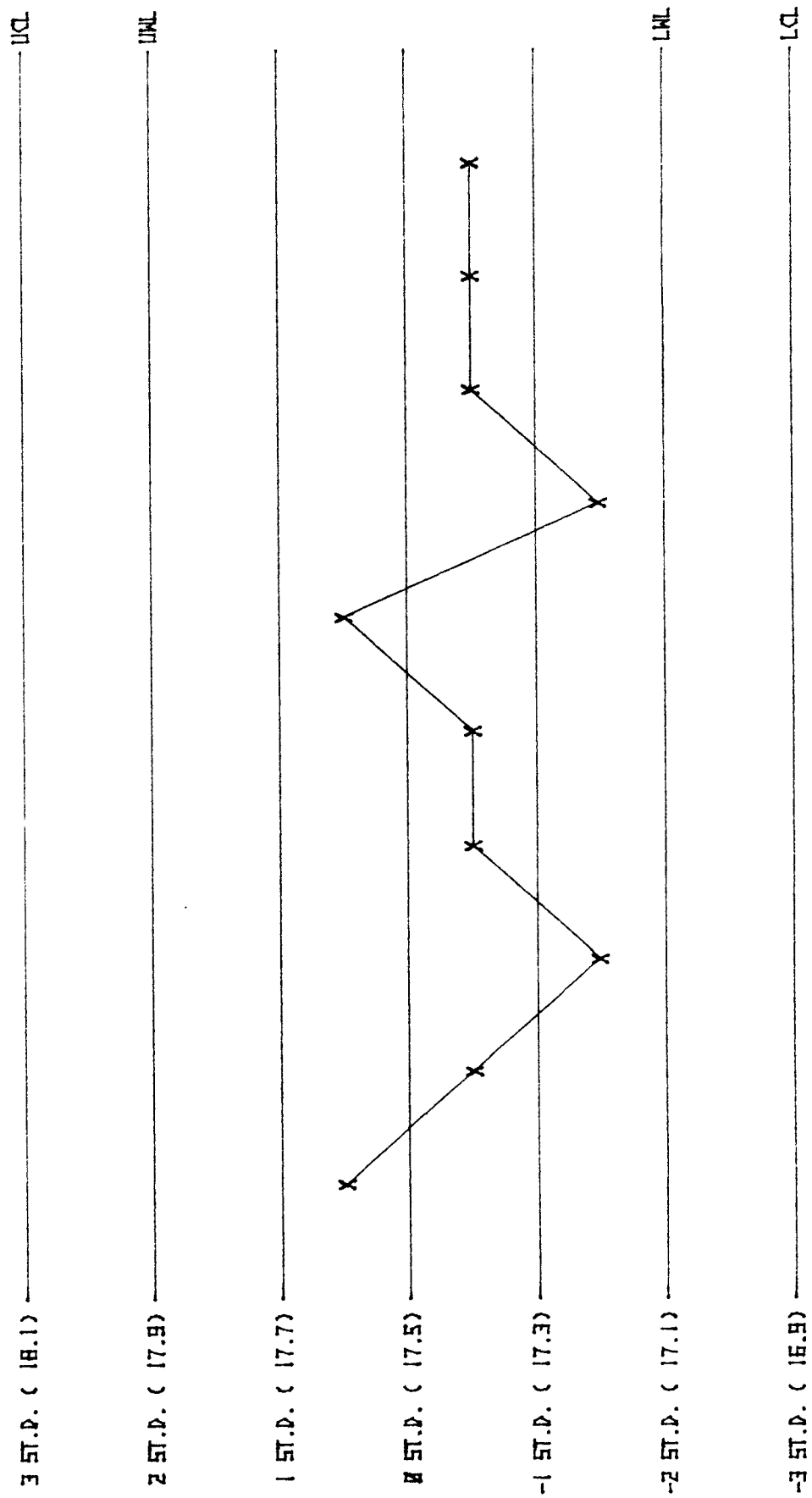
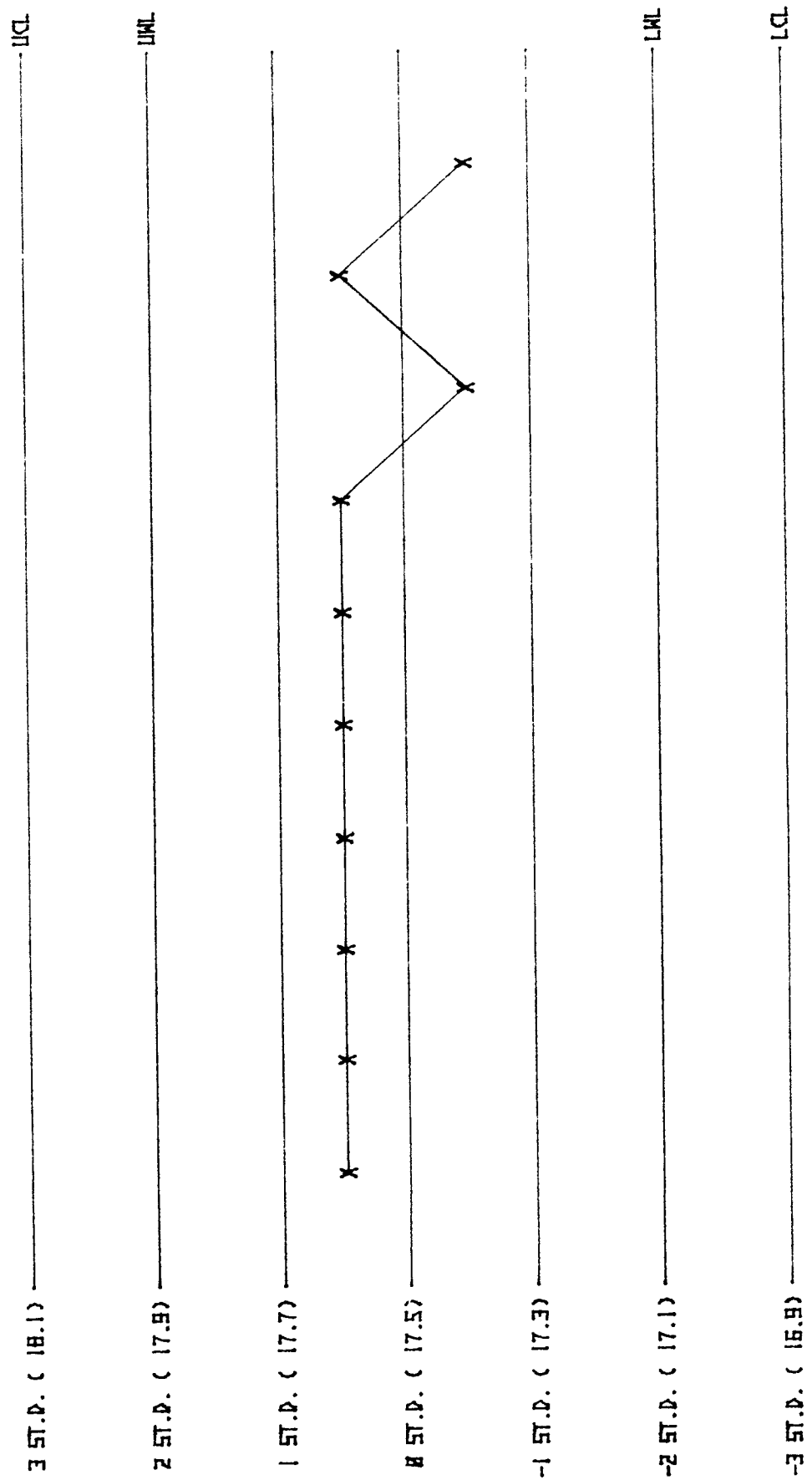


FIGURE 2. CONTROL CHART FOR ZINC IN BLOOD ANALYST: I  
DATE: 12-12-75



# FIGURE 3. CONTROL CHART FOR ZINC IN BLOOD ANALYST: 13

DATE: 12-16-75

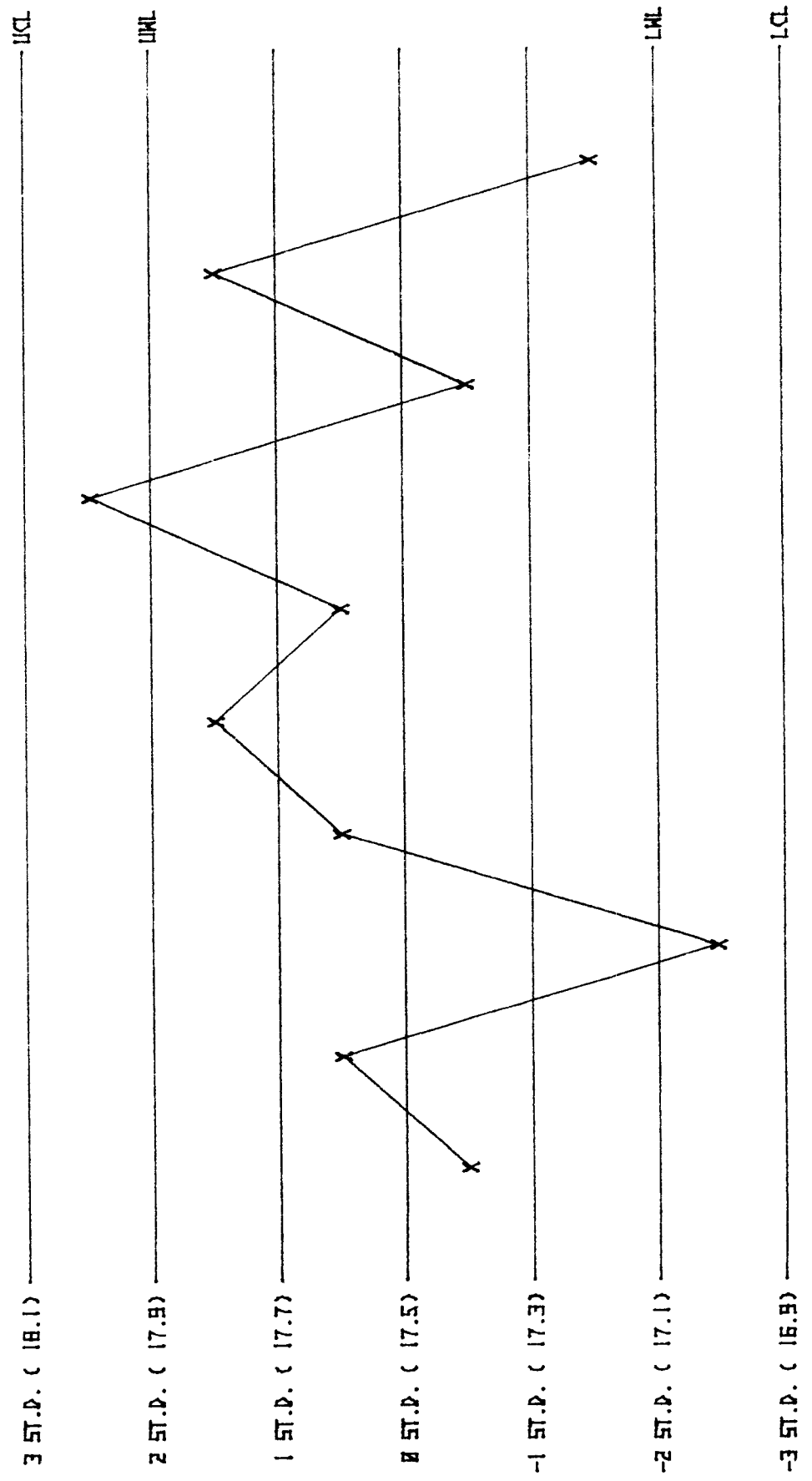


FIGURE 4. CONTROL CHART FOR COPPER IN BLOOD ANALYST: 17  
DATE: 12-11-75

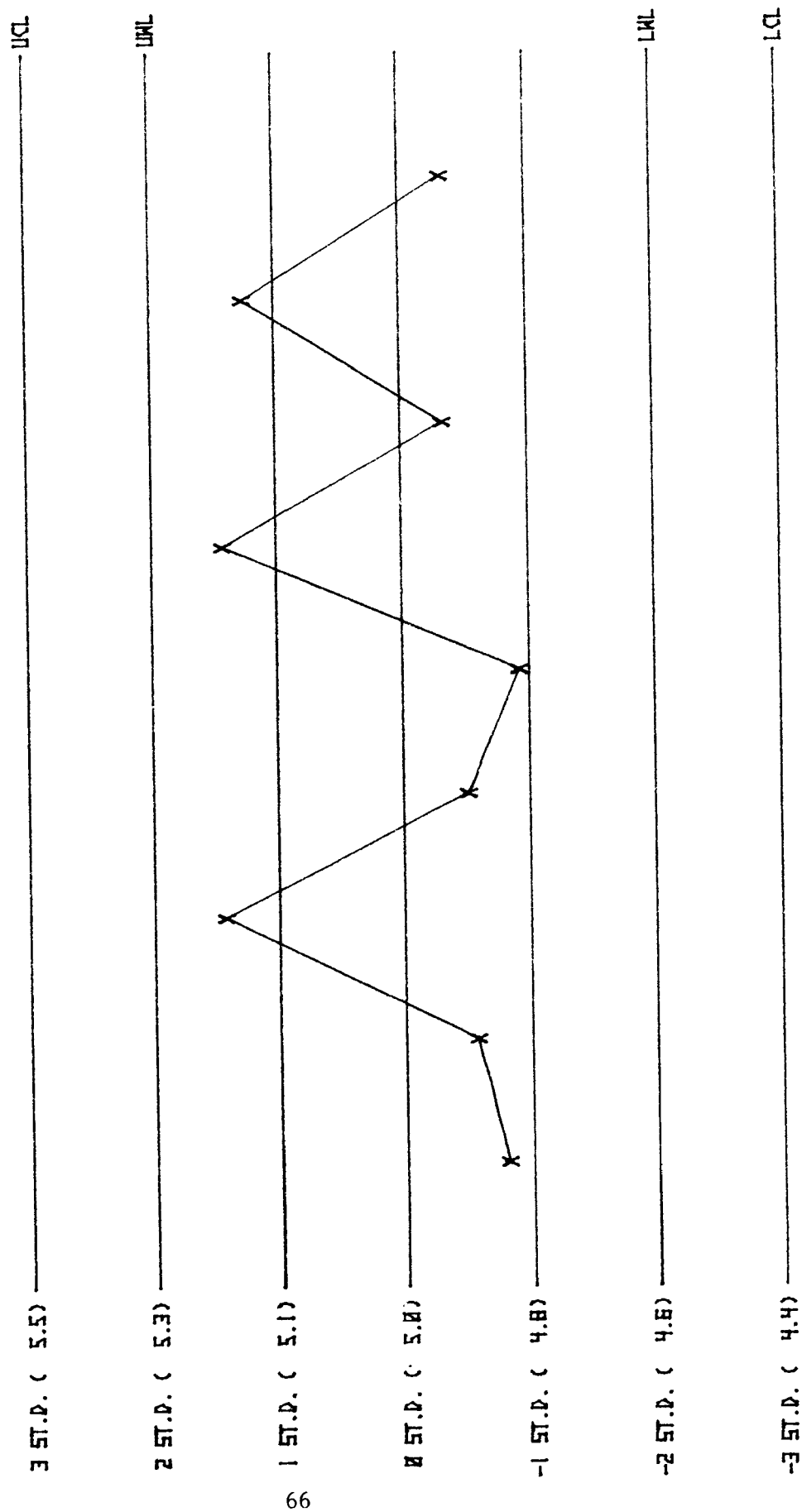


FIGURE 5. CONTROL CHART FOR COPPER IN BLOOD ANALYST: I

DATE: 12-12-75

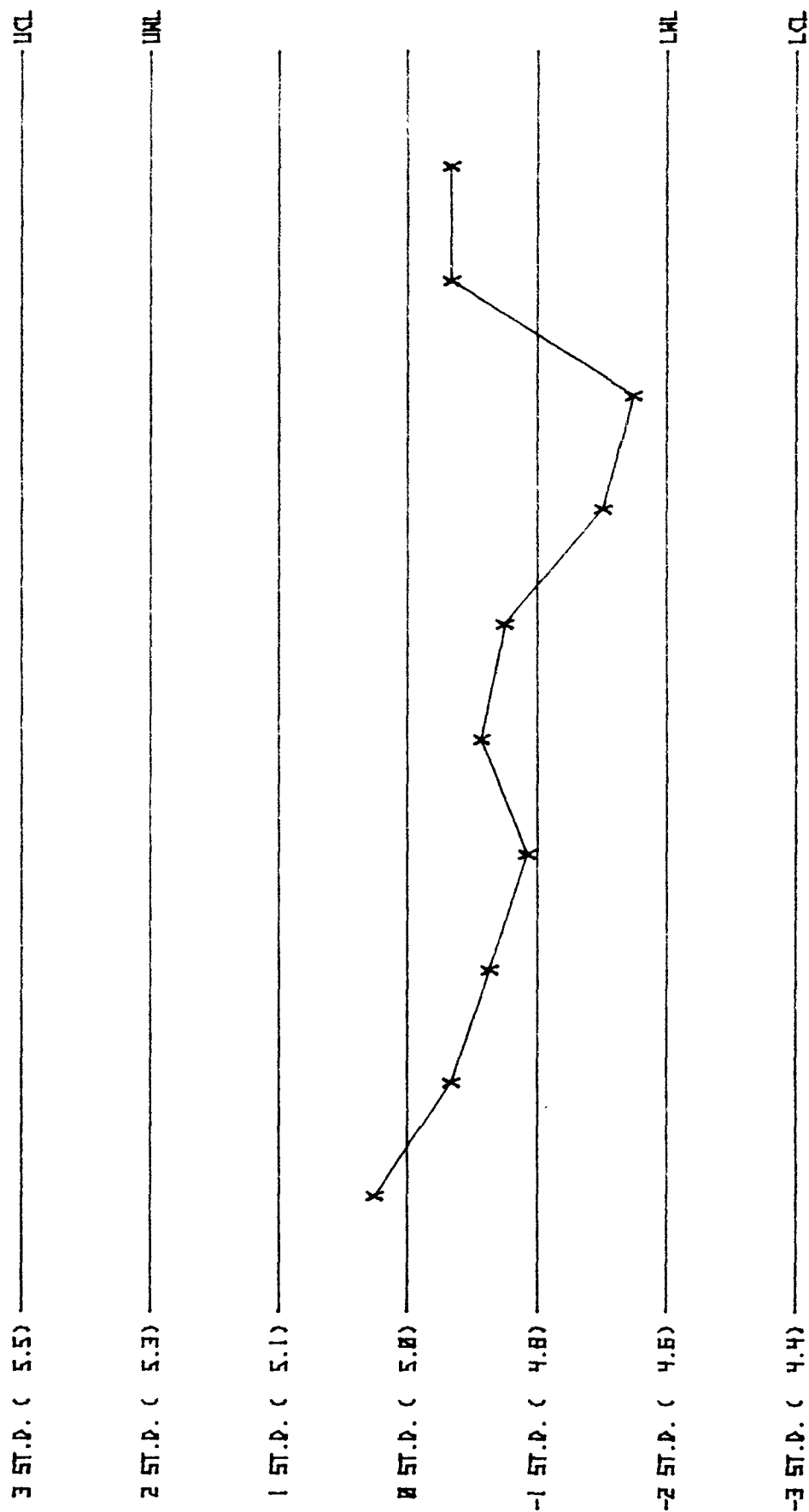




FIGURE 6. CONTROL CHART FOR COPPER IN BLOOD ANALYST: 13  
DATE: 12-16-75

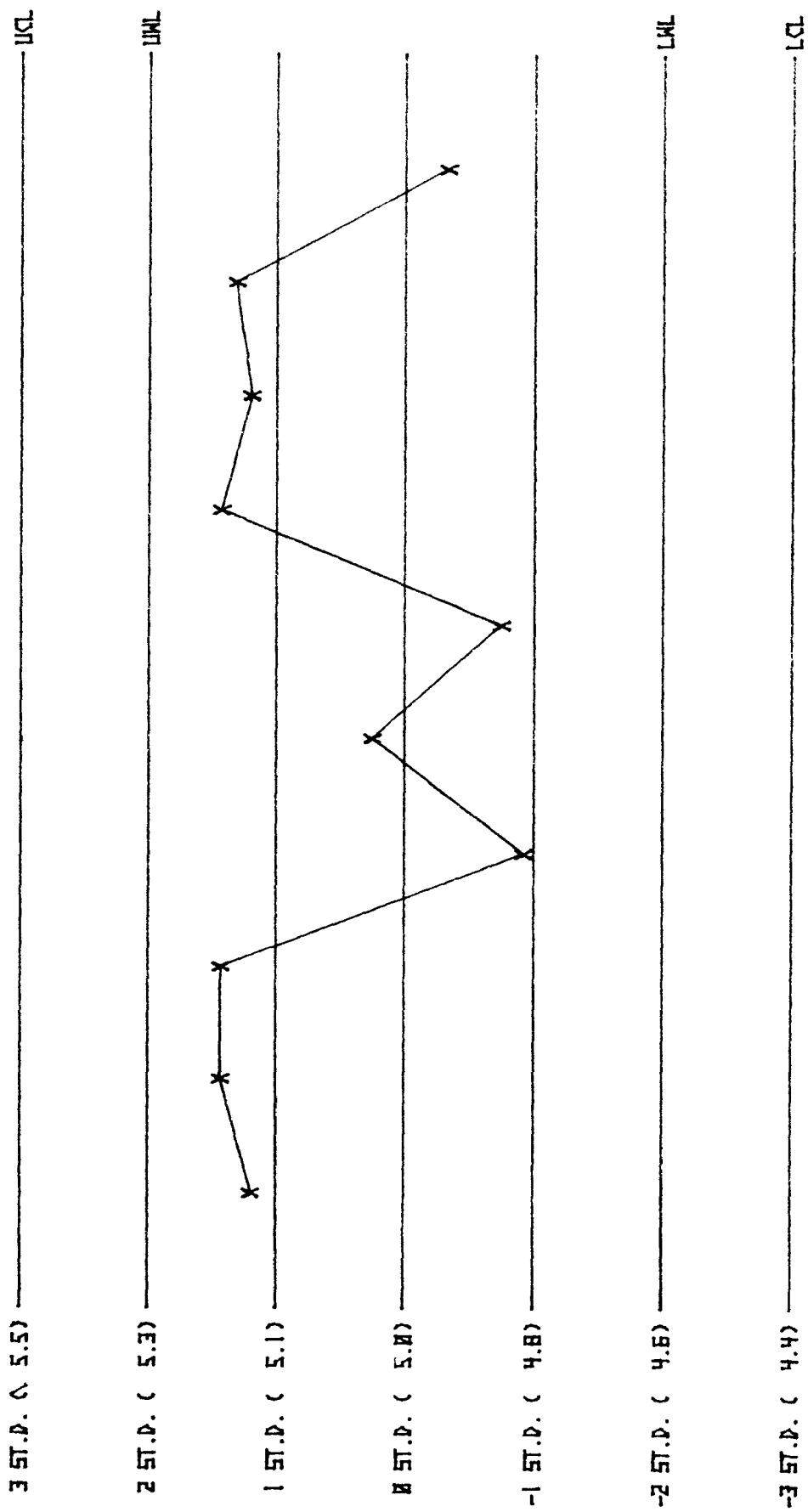


FIGURE 7. CONTROL CHART FOR ARSENIC IN URINE ANALYST: 17  
DATE: 11-19-75

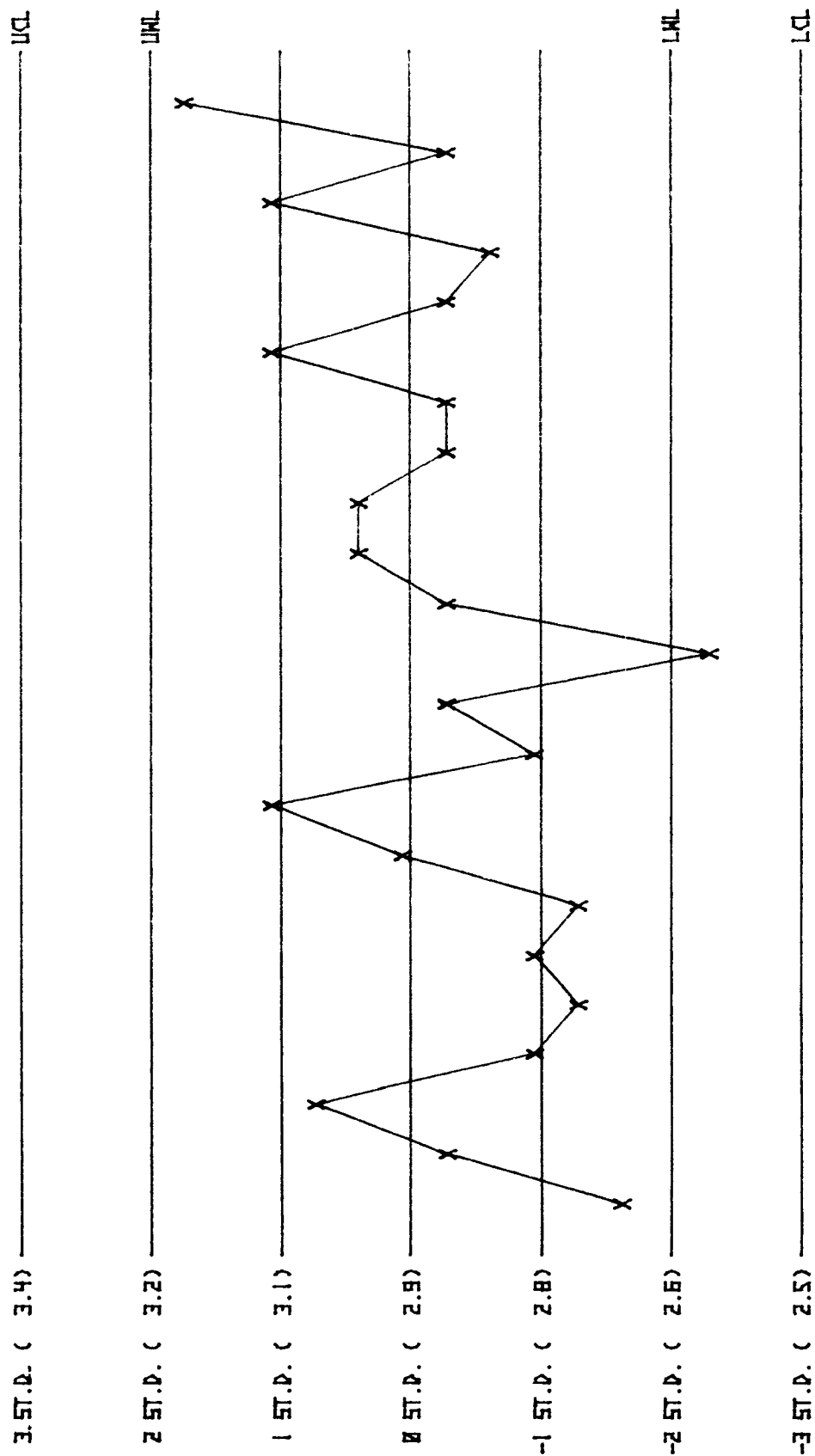


FIGURE B. CONTROL CHART FOR ARSENIC IN URINE ANALYST: 17  
 DATE: 11-20-75

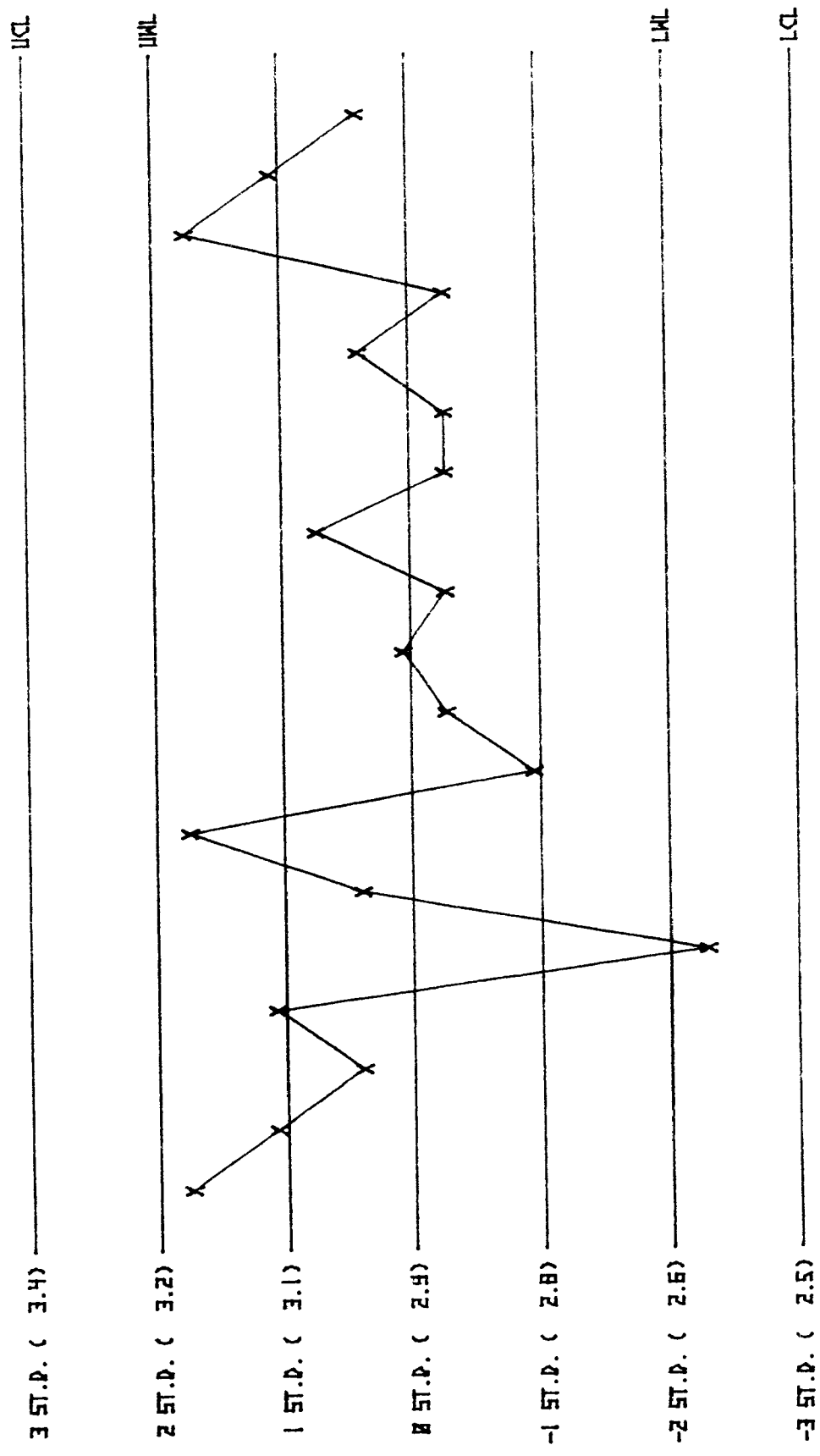


FIGURE 9. CONTROL CHART FOR ARSENIC IN URINE ANALYST: I  
DATE: 12-2-75

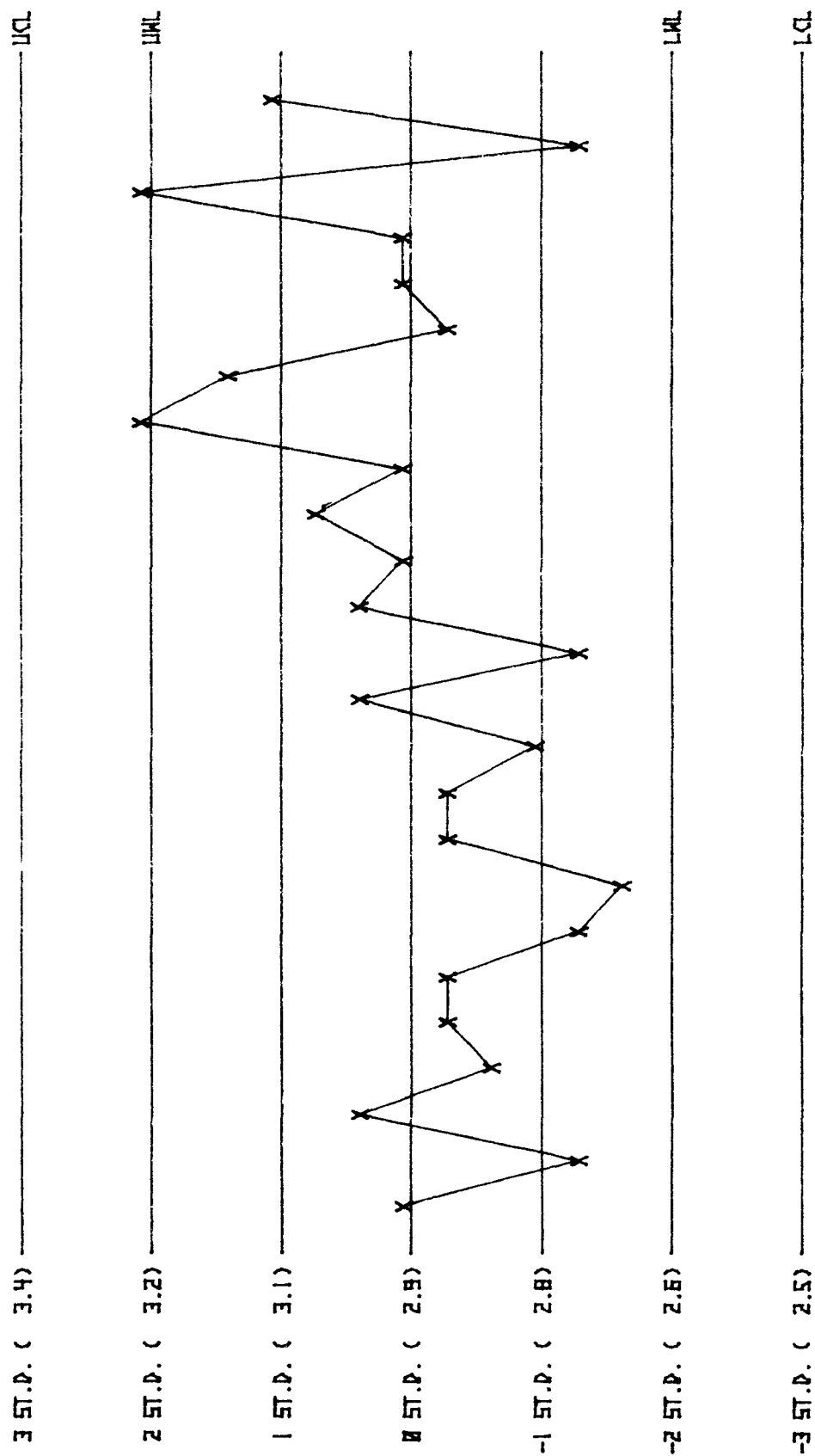


FIGURE 10. CONTROL CHART FOR LEAD IN BLOOD ANALYST: Z AND Z2  
DATE: 12-28-75

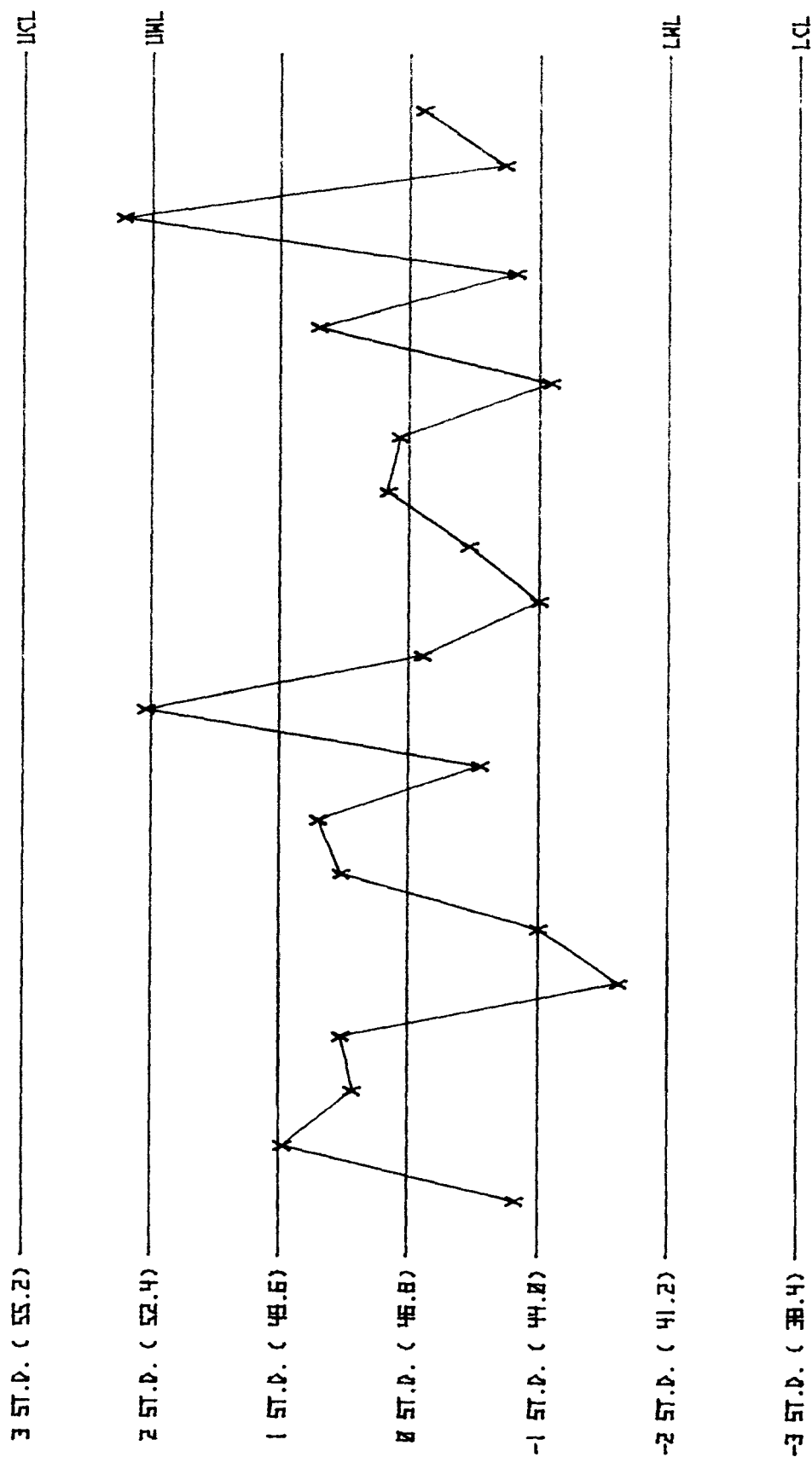


TABLE 10. Summary of Control Chart Data

	<u>Copper (ppm)</u>	<u>Zinc (ppm)</u>	<u>Lead (ppb)</u>	<u>Arsenic (ppb)</u>
Mean	4.96	17.5	46.8	2.94
Standard Deviation abs.	0.17	0.20	2.80	0.15
Uncertainty Limits of Mean				
abs. $\pm$	0.07	$\pm$ 0.08	$\pm$ 1.3	$\pm$ 0.04
(95% Confidence Interval) rel $\pm$	1.31	$\pm$ 0.43	$\pm$ 2.69	$\pm$ 1.24
Coefficient of Variation	3.44%	1.15%	5.98%	5.06%

A comparison of the precision measurements between the 4.49 gm dissolved composite (Table 11) and the ten individual 0.5 gm dry hair aliquots (Table 12) clearly differentiates the reproducibility of the analytical instrumentation, as defined by the former, from the inherent elemental variability in hair, as shown by the latter. These data conclusively demonstrate the significance and magnitude of this variation in trace metal concentrations when small individual hair samples are compared analytically. A comparative summary of these statistical profiles is found in Table 13.

Another study was conducted on a second hair composite. The composite was divided into thirteen individual 0.5 gm samples. These samples were submitted to the laboratory as blind samples in the last three batches of the project. The analytical results are given in Table 14.

Based on these three studies, the innate variability of certain elements in hair was clearly demonstrated. This fact will have a significant bearing on the accurate interpretation of the blind sample split analyses conducted for this contract. This topic will be discussed in detail in a later section of this report.

### 3. Interlaboratory Comparison Analyses

- a. Comparative Arsenic Analyses--Concurrent with this contract effort, the Contractor, was employed by EPA to analyze

TABLE 11. Analytical Data from 10 Aliquots of Composite Hair Sample  
(4.49 grams) - Prepared as One Single Sample.

Concentration units are micrograms per gram

<u>Sample No.</u>	<u>Lead</u>	<u>Cadmium</u>	<u>Arsenic</u>	<u>Copper</u>	<u>Zinc</u>
BB 007-1	10.0	1.45	<0.05	24.3	497.
BB 007-2	10.0	1.50	<0.05	24.6	497.
BB 007-3	10.0	1.45	<0.05	24.4	497.
BB 007-4	9.85	1.45	<0.05	24.6	497.
BB 007-5	9.80	1.45	<0.05	24.3	497.
BB 007-6	9.90	1.45	<0.05	24.3	497.
BB 007-7	10.0	1.45	<0.05	24.3	500.
BB 007-8	10.1	1.45	<0.05	24.3	494.
BB 007-9	10.0	1.50	<0.05	24.6	494.
BB 007-10	10.0	1.45	<0.05	24.3	494.
Mean Value abs. (95% Confidence Interval)	9.97 $\pm$ 0.06	1.46 $\pm$ 0.02	<0.05	24.4 $\pm$ 0.10	496. $\pm$ 4
Standard Deviation, abs.	0.09	0.02		0.14	1.90
Coefficient of Variation	0.90%	1.44%	0	0.58%	0.38



TABLE 12. Analytical Data for Ten Individual 0.5 gram  
Aliquots of Composite Hair Sample

Concentration units are micrograms per gram

<u>Sample No.</u>	<u>Lead</u>	<u>Cadmium</u>	<u>Arsenic</u>	<u>Copper</u>	<u>Zinc</u>
Z 019	8.80	0.67	<0.05	24.9	506.
Z 020	10.0	0.67	<0.05	30.1	593.
Z 021	11.3	1.11	0.10	27.1	521.
Z 022	12.5	1.22	<0.05	27.1	516.
Z 023	10.0	0.67	<0.05	24.6	481.
Z 024	10.0	0.75	0.10	25.9	491.
Z 025	10.0	1.50	0.06	27.1	526.
Z 026	17.5	2.13	<0.05	28.6	518.
Z 027	11.3	1.38	<0.05	25.1	488.
Z 028	10.0	0.88	<0.05	29.1	538.
Mean Value abs. (95% Confidence Interval)	11.1 $\pm$ 1.76	1.10 $\pm$ 0.34	$\leq$ 0.06	27.0 $\pm$ 1.34	518. $\pm$ 22.9
Standard Deviation, abs.	2.46	0.48		1.87	32.
Coefficient of Variation	22.1%	43.4%		6.95%	6.19%

TABLE 13. Summary-Hair Study Precision Data

	<u>Lead</u>	<u>Cadmium</u>	<u>Copper</u>	<u>Zinc</u>
Mean Value, 95%				
Confidence Interval,				
Composite	9.97 $\pm$ 0.06	1.46 $\pm$ 0.02	24.4 $\pm$ 0.10	496 $\pm$ 1.35
Individual	11.1 $\pm$ 1.76	1.10 $\pm$ 0.34	27.0 $\pm$ 1.34	518 $\pm$ 22.9
Standard Deviation				
Composite	0.09	0.02	0.14	1.90
Individual	2.46	0.48	1.87	32.
Coefficient of Variation				
Composite	0.90%	1.44%	0.58%	0.38%
Individual	22.1%	43.4%	6.95%	6.19%

TABLE 14. Analysis of Quality Control Hair Composite No. 2

Concentration units are micrograms per gram

<u>Sample No.</u>	<u>Batch No.</u>	<u>Lead</u>	<u>Cadmium</u>	<u>Arsenic</u>
F 5264	4	5.00	<0.25	0.25
F 5377	4	12.5	0.38	0.075
F 5487	4	11.3	0.25	0.35
F 5578	4	13.8	0.25	N. A.*
F 6727	5	11.3	0.25	0.40
F 6774	5	12.5	0.38	0.33
F 6846	5	11.3	0.25	0.28
F 6920	5	15.0	0.25	N. A.*
F 8270	6	10.0	0.75	0.28
F 8347	6	12.5	0.38	0.28
F 8389	6	11.3	0.75	N. A.*
F 8482	6	10.0	0.25	N. A.*
F 8561	6	7.50	<0.25	0.25
Mean Value abs. (95% Confidence Interval)		11.1 $\pm$ 1.57	0.36 $\pm$ 0.11	
Standard Deviation, abs.		2.6	0.18	0.09
Coefficient of Variation		23.5%	51.3%	32.7%

\*N. A. = Not Analyzed. Sample was controlling a zinc smelter

arsenic in particulate matter. The analytical methodology employed in this effort was NIOSH Method P & CAM 139 (arsenic in urine and air) which is the identical method used for Contract No. 68-02-2266. In the initial phase of the aforementioned project, a correlation study was conducted to compare the NIOSH arsenic method with EPA flameless atomic absorption technique. Results of these analyses on sample splits provided and analyzed by EPA are given in Table 15. The correlation coefficient for these data is 0.9943.

- b. Comparative Blood Lead Analyses--On December 30, 1975, the Contractor received twelve reference blood samples from the Center for Disease Control (CDC). The Contractor analyzed these samples by the graphite furnace atomic absorption technique. In addition, the three samples with the highest lead values were also analyzed by conventional atomic absorption.

A comparison of the data obtained by the Contractor with the CDC standard values is shown in Table 16. Performance evaluation by CDC was based on the following criteria:

For values  $\geq 40 \mu\text{g}/100 \text{ ml}$ ,  $\pm 15\%$

For values  $< 40 \mu\text{g}/100 \text{ ml}$ ,  $\pm 6 \mu\text{g}$

In only one case out of twelve, did the Contractor's data differ from the CDC value by more than  $\pm 6 \mu\text{g}$ . Sample 5-27 differed by  $6.2 \mu\text{g}$ .

- c. Interlaboratory Study Conclusions--Based on the results of

TABLE 15. Comparison of Analytical Results of the NIOSH and EPA Arsenic Methods

Concentrations are micrograms Arsenic per milliliter

<u>Sample No.</u>	<u>Contractor Results (NIOSH Method P &amp; CAM 139)</u>	<u>EPA Results (Flameless AA)</u>
4	2.00	1.7
7	20.0	19.2
12	15.4	19.5
13	1.56	1.6
14	5.60	4.8
15	6.10	6.5
20	44.0	44.8

TABLE 16. Comparative Data - Blood Lead

(Concentrations are expressed as  $\mu\text{g Pb}/100\text{ ml whole blood}$ )

<u>Contractor Code</u>	<u>CDC Code</u>	<u>Contractor Result</u>	<u>CDC Value</u>
GF 6958	5-29	76.6 $\pm$ 3.6	71.8 $\pm$ 4.6
GF 6958*	5-29 Direct Aspiration	76.4 $\pm$ 2.1	
GF 6959	5-18	12.1 $\pm$ 2.1	14.4 $\pm$ 1.9
GF 6960	5-36	25.5 $\pm$ 2.0	26.4 $\pm$ 2.8
GF 6961	5-15	13.4 $\pm$ 1.0	16.3 $\pm$ 2.2
GF 6962	5-12	22.7 $\pm$ 0.8	19.7 $\pm$ 1.7
GF 6963	5-27	38.0 $\pm$ 0.9	31.8 $\pm$ 1.1
GF 6964	5-24	37.2 $\pm$ 1.3	33.2 $\pm$ 1.7
GF 6965	5-35	55.4 $\pm$ 1.0	50.2 $\pm$ 2.6
GF 6965*	5-35 Direct Aspiration	49.1 $\pm$ 1.5	
GF 6966	5-33	40.8 $\pm$ 0.8	37.2 $\pm$ 2.4
GF 6967	5-32	56.1 $\pm$ 0.7	59.4 $\pm$ 3.6
GF 6968	5-30	44.9 $\pm$ 1.0	41.5 $\pm$ 2.6
GF 6969	5-28	78.3 $\pm$ 1.8	79.0 $\pm$ 3.1
GF 6969*	5-28 Direct Aspiration	81.3 $\pm$ 2.0	

\*Direct Aspiration Atomic Absorption Data

A sample of NBS bovine liver was also analyzed with these samples. These results are expressed as  $\mu\text{g Pb}/\text{gram of SRM}$ .

<u>Contractor Code</u>	<u>NBS Code</u>	<u>Contractor Result</u>	<u>NBS Certified Value</u>
GF 6970	SRM 1577	0.33 $\pm$ 0.04	0.34 $\pm$ 0.08

these two interlaboratory comparisons between the Contractor and the reference laboratories of EPA and CDC, it can be concluded that the accuracy data generated by the internal quality control program of the Contractor provide a valid assessment of the quality of the analytical data produced under this contract.

4. Blind Sample Split Analyses--A large portion of the internal analytical quality control program encompassed blind split sample analysis of hair, blood, and urine. A measure of the statistical profile of these data is the coefficient of variation for the split sample pairs. Complete data for this phase of the contract effort are appended. Comparative precision data for the appropriate type of composite control sample and the mean value for the actual sample splits are contained in Table 17. If all pertinent criteria for effective quality control have been satisfied, the Coefficient of Variation should be approximately equal for the control samples and the actual sample splits.

An analysis of the data immediately indicates that some phase of the program is "out of control." The final segment of this report section is devoted to an assessment of the internal analytical quality control program and related ramifications.

5. Assessment of Analytical Quality Control Program--A quality control program in the laboratory has two primary functions. First, the program should monitor the reliability of the results

TABLE 17. Coefficient of Variation Comparison for Control Samples and Mean of Actual Sample Splits.

	<u>V for Control Samples</u>	<u>V for Mean of Actual Sample Splits</u>
<u>Hair</u>		
Lead	5.98%	15.2%
Cadmium	6.15%	17.5%
Arsenic	5.06%	14.8%
<u>Blood</u>		
Lead	5.98%	22.0%
Copper	3.44%	10.6%
Zinc	1.55%	9.0%
FEP	Not Determined	4.51%
<u>Urine</u>		
Arsenic	5.06%	24.9%



reported. It should continually provide an answer to, "How good are the submitted results?" This phase may be termed "measurement of quality." The second function is the control of quality in order to meet the program requirements for reliability.

The control of analytical performance in the laboratory is based on the assumption that a "valid sample" has been submitted for analysis. A "valid sample" implies that the sample was properly taken, preserved, and delivered to the laboratory in a condition appropriate for all analytical techniques to be employed. Further, the validity of controlled analytical performance is dependent upon the use of currently recognized analytical methods substantiated by the recording and reporting of subsequent laboratory results in a systematic, uniform, and permanent fashion. It must be recognized, however, that quality control begins with the sample collection and does not end until the resulting data are reported. The laboratory control of analytical performance is but one essential link in obtaining reliable data. Each single phase of a quality control effort will only be as good as the poorest, least controlled area which has an effect on the results.

A review of the internal analytical quality control program precision, accuracy, and interlaboratory comparison data on standard samples revealed that all phases of the analytical performance in the laboratory were "under control." Based on the data from the composite hair study and visual observations of

the blood and urine samples as they were received in the laboratory, the "out of control" portion of the project was readily identifiable as the samples themselves. Analytical quality control is based on the assumption that a homogeneous sample, free from obvious external contamination, has been analyzed. All urine samples received for analysis contained varying amounts of precipitate, and many of the blood samples contained macroclots. Hair samples have an inherent variability and cannot be considered homogeneous tissue samples. In addition, the hair samples were extremely small; and most split analyses were performed on samples sizes of  $\sim 0.25$  gm.

When all pertinent factors are considered, it can be concluded that the Coefficients of Variation obtained for the blind sample splits represent sample inhomogeneity rather than the nonreproducibility of precision for the analytical methodology. This conclusion is in no way detrimental to the internal analytical quality control program. It does, in fact, demonstrate that the program was properly designed and conducted since the "out of control" fraction was isolated and identified.

- E. Assessment of Analytical Data - The problem of less than ideal samples was readily apparent as soon as the first shipment of samples arrived in the laboratory. Appropriate method modification to minimize the overall effect on the project were suggested by the Contractor and approved by the Project Officer. These modifications were designed to overcome sample shortcomings in all areas except those which were

exclusively dependent on sample homogeneity--specifically, blind sample split precision. An overall assessment of the analytical data for each sample type will now be presented.

1. Hair--With the exception of the samples used in the blind split quality control program, the total hair sample as received was analyzed. The uncertainty of the data obtained from those samples which were analyzed in their entirety (>90%) and not split for quality control, correlates directly to the accuracy and precision of the analytical method as previously presented. The mean value for the blind sample split analyses is the most accurate representation for these samples. This mean value has a comparable accuracy to the samples which were analyzed as a whole.
2. Blood--The situation for blood is identical to that for hair.
3. Dust--All dust samples were analyzed as total sample received. On an absolute basis, the data are as good as the accuracy and precision of the methods employed .
4. Urine--The urine analyses are the least precise data in the entire study. Because of an extreme variation in sample size, it was not analytically feasible to perform the analyses on the total sample as received. The nature and amount of precipitate changed drastically from sample to sample. Every effort was made to remove a representative aliquot for analysis; however, the magnitude of the Coefficient of Variation for the blind sample splits

(24.9%) indicates that the difficulty was not overcome in many cases. While the urine data are less precise on an absolute basis, it should be pointed out that on a relative basis the data are still meaningful for collection site comparisons. For example, the median value for arsenic in urine for site AJ is 9.77  $\mu\text{g}/100\text{ ml}$ , for site HA, 3.06  $\mu\text{g}/100\text{ ml}$ , and for site PV, 0.49  $\mu\text{g}/100\text{ ml}$ . Thus it is apparent that the lack of precision in the urine data definitely does not preclude assessment of the relative significance of the analytical results for the study. It should, however, be pointed out that the validity of specific gravity measurements taken on precipitated samples has not been established.

The measures of accuracy formulated in section D of this report can be applied directly to an evaluation of all data for a given element analyzed in a specific matrix. A summary treatment of the analytical means of each type of determination for the four matrices from various collection sites is shown in Tables 18 through 21. The accuracy of these values, and the individual data from which they were generated, is basically equivalent to that achieved analytically on standard reference materials.

In the past, it has been customary to exclude "less-than" values from chemical analytical data before performing statistical analysis. This is regrettable as the less-than values may reflect the condition of an important subset of the data, and their omission possibly precludes the likelihood that the finished

TABLE 18. Analytical Data Summary - Hair

Concentration units are micrograms per gram

"Range indicated is the mean  $\pm$  2 standard deviations"

<u>Collection Site</u>	<u>Lead</u>	<u>Cadmium</u>	<u>Arsenic</u>
AJ	19.2 $\pm$ 0.3	2.68 $\pm$ 0.08	1.91 $\pm$ 0.19
AL	17.5 $\pm$ 0.3	0.69 $\pm$ 0.02	0.10 $\pm$ 0.01
AM	38.4 $\pm$ 0.7	4.11 $\pm$ 0.12	
AN	25.4 $\pm$ 0.5	1.94 $\pm$ 0.06	20.3 $\pm$ 2.1
AP	23.5 $\pm$ 0.4	2.22 $\pm$ 0.06	0.48 $\pm$ 0.05
BV	56.7 $\pm$ 1.	9.14 $\pm$ 0.26	
BX	170. $\pm$ 3.	7.94 $\pm$ 0.23	
CC	45.8 $\pm$ 0.8	2.78 $\pm$ 0.08	
CH	22.8 $\pm$ 0.4	2.80 $\pm$ 0.08	0.14 $\pm$ 0.02
DO	26.7 $\pm$ 0.5	1.88 $\pm$ 0.05	0.43 $\pm$ 0.04
GL	51.1 $\pm$ 0.9	6.35 $\pm$ 0.18	
HA	26.4 $\pm$ 0.5	1.81 $\pm$ 0.05	2.09 $\pm$ 0.21
HK	64.0 $\pm$ 1.	4.26 $\pm$ 0.12	
HL	20.4 $\pm$ 0.4	1.65 $\pm$ 0.05	0.18 $\pm$ 0.02
MG	15.9 $\pm$ 0.3	1.33 $\pm$ 0.04	0.37 $\pm$ 0.04
MI	31.7 $\pm$ 0.6	1.90 $\pm$ 0.06	0.47 $\pm$ 0.05
MN	20.4 $\pm$ 0.4	2.13 $\pm$ 0.06	
MO	17.6 $\pm$ 0.3	1.96 $\pm$ 0.06	0.31 $\pm$ 0.03
NG	15.9 $\pm$ 0.3	1.29 $\pm$ 0.04	0.41 $\pm$ 0.04
PL	44.4 $\pm$ 0.8	7.40 $\pm$ 0.21	
PV	12.6 $\pm$ 0.2	1.18 $\pm$ 0.03	0.09 $\pm$ 0.01
SA	11.9 $\pm$ 0.2	1.09 $\pm$ 0.03	0.10 $\pm$ 0.01
SM	19.3 $\pm$ 0.3	1.26 $\pm$ 0.04	0.23 $\pm$ 0.02
WP	13.9 $\pm$ 0.3	1.84 $\pm$ 0.05	0.43 $\pm$ 0.04
All Sites	29.3 $\pm$ 0.5	2.95 $\pm$ 0.08	2.14 $\pm$ 0.22
Number of Positive Results	1577	1451	1126

TABLE 19. Analytical Data Summary - Blood

Concentrations are  $\mu\text{g}/100\text{ ml}$  whole blood"Range indicated is the mean  $\pm$  2 standard deviations"

Collection Site	FEP	Lead	Cadmium	Copper	Zinc
AJ	22.1 $\pm$ 1.7	12.5 $\pm$ 2.0		105. $\pm$ 7.	372. $\pm$ 18.
AL	26.1 $\pm$ 2.0	17.7 $\pm$ 2.8	0.21 $\pm$ 0.03	99.4 $\pm$ 7.	368. $\pm$ 18.
AM	28.8 $\pm$ 2.2	22.7 $\pm$ 3.6	0.12 $\pm$ 0.02		371. $\pm$ 18.
AN	26.8 $\pm$ 2.1	13.4 $\pm$ 2.1		90.3 $\pm$ 6.	372. $\pm$ 18.
AP	35.8 $\pm$ 2.8	19.6 $\pm$ 3.1		95.7 $\pm$ 6.	320. $\pm$ 16.
BV	26.5 $\pm$ 2.1	28.9 $\pm$ 4.6	0.51 $\pm$ 0.07		552. $\pm$ 27.
BX	33.9 $\pm$ 2.6	13.7 $\pm$ 2.2	0.12 $\pm$ 0.02		
CC	28.6 $\pm$ 2.2	19.6 $\pm$ 3.1	0.16 $\pm$ 0.02		295. $\pm$ 15.
CH	18.5 $\pm$ 1.4	16.5 $\pm$ 2.6		97.7 $\pm$ 6.	346. $\pm$ 17.
DO	30.0 $\pm$ 2.3	20.5 $\pm$ 3.3		94.6 $\pm$ 6.	339. $\pm$ 17.
GL	22.2 $\pm$ 1.7	12.6 $\pm$ 2.0	0.16 $\pm$ 0.02		
HA	30.4 $\pm$ 2.4	21.2 $\pm$ 3.4		152. $\pm$ 10.	521. $\pm$ 26.
HK	26.8 $\pm$ 2.1	18.8 $\pm$ 3.0	0.32 $\pm$ 0.05		
HL	34.1 $\pm$ 2.7	17.1 $\pm$ 2.7		75.5 $\pm$ 5.	383. $\pm$ 19.
MG	19.4 $\pm$ 1.5	9.1 $\pm$ 1.5		96.6 $\pm$ 6.	352. $\pm$ 17.
MI	27.3 $\pm$ 2.1	17.3 $\pm$ 2.8		126. $\pm$ 8.	424. $\pm$ 21.
MN	25.9 $\pm$ 2.0	14.8 $\pm$ 2.4	0.22 $\pm$ 0.03		351. $\pm$ 17.
MO	23.8 $\pm$ 1.8	13.9 $\pm$ 2.2		106. $\pm$ 7.	340. $\pm$ 17.
NG	37.0 $\pm$ 2.9	15.3 $\pm$ 2.4	0.29 $\pm$ 0.04	104. $\pm$ 7.	352. $\pm$ 17.
PL	35.6 $\pm$ 2.7	17.9 $\pm$ 2.9	0.37 $\pm$ 0.05		362. $\pm$ 18.
PV	21.0 $\pm$ 1.6	16.9 $\pm$ 2.7	0.24 $\pm$ 0.03	92.7 $\pm$ 6.	372. $\pm$ 18.
SA	23.1 $\pm$ 1.8	15.2 $\pm$ 2.4	0.18 $\pm$ 0.03	78.1 $\pm$ 5.	346. $\pm$ 17.
SM	23.8 $\pm$ 1.9	18.0 $\pm$ 2.9		106. $\pm$ 7.	362. $\pm$ 18.
WP	17.3 $\pm$ 1.3	18.6 $\pm$ 3.0		106. $\pm$ 7.	374. $\pm$ 18.
All Sites	27.1 $\pm$ 2.1	17.5 $\pm$ 2.8	0.26 $\pm$ 0.04	103. $\pm$ 7.	379. $\pm$ 19.
Number of Positive Results	1941	1921	844	1392	1762

TABLE 20. Analytical Data Summary - Dust

Concentrations are absolute micrograms per towlette

"Range indicated is the mean  $\pm$  2 standard deviations"

Collection Site	Lead	Cadmium	Arsenic	Copper	Zinc
AJ	44.2 $\pm$ 0.8	1.73 $\pm$ 0.05	3.97 $\pm$ 0.4	128. $\pm$ 1.5	260. $\pm$ 2.
AL	17.7 $\pm$ 0.4	0.88 $\pm$ 0.03	0.09 $\pm$ 0.009	559. $\pm$ 6.	96.6 $\pm$ 0.7
AM	35.9 $\pm$ 0.6	1.50 $\pm$ 0.04	0.50 $\pm$ 0.05	423. $\pm$ 5.	241. $\pm$ 1.8
AN	45.2 $\pm$ 0.8	2.22 $\pm$ 0.06	34.2 $\pm$ 3.4	122. $\pm$ 1.4	111. $\pm$ 0.8
AP	48.4 $\pm$ 0.9	1.34 $\pm$ 0.04	1.18 $\pm$ 0.12	123 $\pm$ 1.4	89.7 $\pm$ 0.7
BV	76.2 $\pm$ 1.4	8.64 $\pm$ 0.25	0.77 $\pm$ 0.08	17.6 $\pm$ 0.2	546. $\pm$ 4.
BX	293. $\pm$ 5.3	0.49 $\pm$ 0.01	0.27 $\pm$ 0.03	2.14 $\pm$ 0.03	114. $\pm$ 0.9
CC					
CH	82.5 $\pm$ 1.5	1.74 $\pm$ 0.05	0.40 $\pm$ 0.04	78.1 $\pm$ 0.9	149. $\pm$ 1.1
DO	142. $\pm$ 2.6	2.86 $\pm$ 0.08	3.67 $\pm$ 0.37	462. $\pm$ 5.4	192. $\pm$ 1.5
GL	37.5 $\pm$ 0.7	0.71 $\pm$ 0.02	0.09 $\pm$ 0.009	123. $\pm$ 1.4	43.8 $\pm$ 0.33
HA	56.4 $\pm$ 1.0	2.35 $\pm$ 0.07	8.93 $\pm$ 0.9	709. $\pm$ 8.	471. $\pm$ 4.
HK	81.0 $\pm$ 1.5	1.18 $\pm$ 0.03	0.12 $\pm$ 0.01	1023 $\pm$ 12.	179. $\pm$ 1.4
HL	44.1 $\pm$ 0.8	0.61 $\pm$ 0.02	0.27 $\pm$ 0.03	408. $\pm$ 5.	50.2 $\pm$ 0.38
MG	17.4 $\pm$ 0.3	0.82 $\pm$ 0.02	0.91 $\pm$ 0.09	56.9 $\pm$ 0.7	39.3 $\pm$ 0.30
MI	19.6 $\pm$ 0.4	0.85 $\pm$ 0.02	0.56 $\pm$ 0.06	107. $\pm$ 1.2	110. $\pm$ 0.83
MN					
MO	22.2 $\pm$ 0.4	1.51 $\pm$ 0.04	0.41 $\pm$ 0.04	158. $\pm$ 1.8	275. $\pm$ 2.
NG	37.4 $\pm$ 0.7	0.92 $\pm$ 0.03	1.43 $\pm$ 0.14	63.2 $\pm$ 0.7	98.3 $\pm$ 0.7
PL	86.1 $\pm$ 1.6	10.3 $\pm$ 0.30	2.35 $\pm$ 0.24	140. $\pm$ 1.6	1616. $\pm$ 12.
PV	25.2 $\pm$ 0.5	1.23 $\pm$ 0.04	0.15 $\pm$ 0.02	2.73 $\pm$ 0.03	60.0 $\pm$ 0.5
SA	24.1 $\pm$ 0.4	1.14 $\pm$ 0.03	0.31 $\pm$ 0.03	21.3 $\pm$ 0.25	145. $\pm$ 1.1
SM	25.5 $\pm$ 0.5	0.42 $\pm$ 0.01	0.41 $\pm$ 0.04	35.3 $\pm$ 0.41	40.7 $\pm$ 0.3
WP	50.2 $\pm$ 0.9	1.51 $\pm$ 0.04	0.44 $\pm$ 0.04	1784. $\pm$ 21.	434. $\pm$ 3.
All Sites	59.8 $\pm$ 1.1	2.10 $\pm$ 0.06	2.87 $\pm$ 0.29	295. $\pm$ 3.	247. $\pm$ 2.
Number of Positive Results	220	220	214	220	219

TABLE 21. Analytical Data Summary - Urine

Concentrations are micrograms As/100 ml

Collection Sites	Mean Coefficient of Variation	Mean Value	Uncertainty* Calculated Using	
			Actual Site V	Mean V for Project
AJ	10.8%	11.53	$\pm 2.5$	$\pm 5.7$
AL	30.6%	1.33	$\pm 0.8$	$\pm 0.7$
AN	12.3%	3.82	$\pm 0.9$	$\pm 1.9$
AP	24.7%	2.19	$\pm 1.1$	$\pm 1.1$
CH	10.5%	2.19	$\pm 0.5$	$\pm 1.1$
DO	38.2%	2.75	$\pm 2.1$	$\pm 1.4$
HA	16.5%	3.81	$\pm 1.3$	$\pm 1.9$
HL	33.5%	1.19	$\pm 0.5$	$\pm 0.6$
MG	22.8%	2.41	$\pm 1.1$	$\pm 1.2$
MI	15.4%	2.53	$\pm 0.8$	$\pm 1.3$
MO	3.9%	2.28	$\pm 0.2$	$\pm 1.1$
NG	16.9%	2.30	$\pm 0.8$	$\pm 1.1$
PV	61.9%	1.34	$\pm 1.7$	$\pm 0.7$
SA	43.5%	1.90	$\pm 1.7$	$\pm 0.9$
SM	27.7%	2.80	$\pm 1.6$	$\pm 1.4$
WP	20.7%	2.50	$\pm 1.0$	$\pm 1.2$
All Sites	24.9%	3.07		$\pm 1.5$
Number of Positive Results	1034			

\*Uncertainty measurements indicate tolerance limits of  $\pm$  two standard deviations.



statistics are representative of the population from which the samples were taken. A technique exists for working with data having less-thans all of the same value (i.e. truncated data), but no technique has been established for analyzing data having variable less-thans.

If all less-thans are considered to be in fact zero, a mean taken from the data is a low bound on all possible means that may be taken from the data by any technique. Similarly, if the less--thans are considered positive at the value stated for the less-than value, a high bound on the mean may be set. The mean best fitting the data must lie between these two extremes.

The data in Tables 18-22 have been treated in the customary manner. A comparison of the means determined from consideration of only positive results and the means determined by the high and low bounds on these groups of data in which less-than values appeared is contained in Table 22. For most of the data from this study, the calculation of a mean from only positive results produces very little alteration of the population representation.

TABLE 22. Mean Ranges of Groups Containing Less-than Values

<u>Collection Site</u>	<u>Sample Type</u>	<u>Element</u>	<u>Mean of Positives</u>	<u>Mean High Bound</u>	<u>Mean Low Bound</u>
AJ	Hair	Cd	2.684	2.660	2.653
AJ	Hair	Pb	19.185	18.850	18.739
AL	Dust	As	0.090	0.077	0.072
AL	Hair	As	0.096	0.089	0.083
AL	Hair	Cd	0.690	0.486	0.390
AL	Urine	As	1.328	1.231	1.223
AM	Blood	Cd	0.120	0.117	0.115
AM	Hair	Cd	4.118	3.562	3.501
AN	Hair	Cd	1.943	1.868	1.854
AP	Hair	As	0.477	0.467	0.464
AP	Hair	Cd	2.224	2.030	1.983
AP	Hair	Pb	23.450	23.202	23.133
AP	Urine	As	2.187	2.131	2.129
BV	Blood	Cd	0.508	0.502	0.501
BV	Blood	Pb	28.909	28.624	28.577
BX	Dust	As	0.271	0.222	0.217
CC	Hair	Cd	2.779	2.536	2.486
CH	Hair	As	0.144	0.139	0.133
CH	Hair	Cd	2.803	2.718	2.712
CH	Urine	As	2.185	2.057	2.051
DO	Hair	As	0.430	0.426	0.425
DO	Hair	Cd	1.876	1.733	1.699
DO	Hair	Pb	26.739	25.985	25.895
GL	Blood	Pb	12.559	12.091	12.013
GL	Dust	As	0.094	0.087	0.084
GL	Dust	Zn	43.817	39.443	39.436
GL	Hair	Pb	51.161	49.636	49.456
HA	Hair	As	2.086	2.066	2.066
HA	Urine	As	3.812	3.723	3.721
HK	Dust	As	0.117	0.108	0.105
HL	Hair	As	0.183	0.174	0.169
HL	Hair	Cd	1.647	1.474	1.437
HL	Urine	As	1.193	1.135	1.130
MG	Hair	As	0.369	0.357	0.354
MG	Hair	Cd	1.330	0.860	0.679

TABLE 22. Mean Ranges of Groups Containing Less-than Values  
(con't)

<u>Collection Site</u>	<u>Sample Type</u>	<u>Element</u>	<u>Mean of Positives</u>	<u>Mean High Bound</u>	<u>Mean Low Bound</u>
MG	Hair	Pb	15.888	14.570	14.197
MI	Urine	As	2.531	2.463	2.461
MN	Blood	Cd	0.223	0.220	0.220
MO	Urine	As	2.281	2.252	2.251
NG	Hair	As	0.410	0.391	0.385
NG	Hair	Cd	1.289	0.878	0.664
NG	Hair	Pb	15.922	15.393	15.209
NG	Urine	As	2.301	2.208	2.204
PL	Hair	Cd	7.389	7.294	7.289
PV	Dust	As	0.154	0.128	0.123
PV	Hair	As	0.092	0.082	0.075
PV	Hair	Cd	1.176	1.049	1.026
PV	Urine	As	1.340	1.049	1.025
SA	Hair	As	0.100	0.100	0.096
SA	Hair	Cd	0.092	0.972	0.945
SA	Hair	Pb	11.861	11.672	11.633
SA	Urine	As	1.902	1.728	1.718
SM	Hair	As	0.228	0.189	0.163
SM	Hair	Cd	1.262	0.990	0.811
SM	Hair	Pb	19.318	15.182	13.799
WP	Hair	As	0.428	0.419	0.417
WP	Hair	Cd	1.844	1.574	1.525
WP	Hair	Pb	13.907	13.348	13.220
WP	Urine	As	2.502	2.462	2.460

# APPENDIX - QUALITY CONTROL

## FEP

### BLOOD

QC SAMPLE	FP CONC.	CORR. SAMPLE	FP CONC.	COEFFICIENT OF VARIATION		SILVER
				Mean	Standard Dev.	
F299	12.5	GF3989	13.1	13.3	2.48	NO
F300	17.5	GF4001	17.2	17.1	0.95	NO
F301	26.6	GF4017	26.6	26.7	0	NO
F302	11.8	GF4029	9.98	10.9	11.9	NO
F303	27.7	GF4041	25.4	26.5	6.04	NO
F304	24.7	GF4053	24.5	24.6	0.65	NO
F305	23.6	GF4071	25.2	24.4	4.60	NO
F306	24.5	GF4083	24.9	24.5	1.30	NO
F307	12.4	GF4101	34.0	31.2	3.38	NO
F308	19.0	GF4113	19.0	19.0	0	NO
F309	25.3	GF4125	25.8	25.5	1.80	NO
F310	13.8	GF4143	14.1	13.7	1.15	NO
F311	13.5	GF4161	17.7	15.7	6.90	NO
F312	24.0	GF4179	22.7	23.4	4.12	NO
F313	13.7	GF4203	14.7	14.0	4.88	NO
F314	16.9	GF4215	16.2	16.6	1.02	NO
F315	28.1	GF4233	17.9	16.8	8.22	NO
F316	14.0	GF2511	13.1	12.5	5.05	NO
F317	28.2	GF2502	26.6	27.1	1.43	NO
F318	24.5	GF2517	26.6	26.6	0.14	NO
F319	23.4	GF2536	24.5	23.7	3.29	NO
F320	11.1	GF2547	12.8	12.0	0.87	NO
F321	10.6	GF2565	10.4	10.5	1.55	NO
F322	24.6	GF2578	26.3	25.2	8.19	NO
F323	14.4	GF2590	13.0	13.7	2.19	NO
F324	23.5	GF2897	24.3	24.3	4.20	NO
F325	20.7	GF2831	24.9	25.3	10.1	NO
F326	15.3	GF2843	14.6	15.1	2.24	NO
F327	13.5	GF2855	20.1	19.5	1.70	NO
F328	45.5	GF2867	41.7	45.5	6.32	NO
F329	17.2	GF2880	16.8	17.0	1.99	NO
F330	15.9	GF2891	16.3	16.4	3.92	NO
F331	16.4	GF2812	18.0	17.3	0.45	NO
F332	26.9	GF2631	26.9	26.9	0	NO
F333	26.0	GF2660	27.0	27.9	2.52	NO
F334	24.1	GF2671	23.7	23.9	1.40	NO
F335	10.2	GF2689	11.8	11.3	5.50	NO
F336	14.9	GF2701	19.2	17.5	0	NO
F337	22.2	GF2725	25.5	23.2	8.80	NO
F338	17.0	GF2737	19.5	17.7	5.68	NO
F339	26.6	GF2749	21.0	20.7	5.61	NO
F340	11.7	GF2767	15.3	15.7	3.12	NO
F341	24.3	GF2779	15.4	15.7	1.86	NO
F412	4.4	GF4864	25.6	25.7	5.35	NO
F430	11.0	GF4877	23.1	22.7	1.95	NO

# APPENDIX - QUALITY CONTROL

## FEP

## BLOOD

QC SAMPLE	FP CONC.	CORR. SAMPLE	FP CONC.	DIFFERENCE OF		SAMPLE
				NEED	MEASUREMENT	
F421	13.7	GF4883	15.2	14.0	6.90	AN
F422	17.1	GF4890	20.4	18.7	12.5	AN
F423	18.0	GF4897	17.5	17.7	1.86	AN
F424	18.0	GF4899	18.7	19.4	2.79	AN
F425	44.1	GF4903	43.6	43.9	0.77	AN
F426	18.7	GF4913	21.1	19.0	8.42	AN
F427	14.1	GF4931	13.7	13.9	1.34	MC
F428	13.9	GF4933	13.9	13.4	4.84	MC
F429	23.0	GF4938	23.5	23.3	1.40	MC
F430	14.9	GF4951	15.3	15.1	2.00	MC
F431	23.5	GF4954	21.3	22.1	6.94	MC
F432	16.5	GF4969	17.0	17.0	2.29	MC
F433	15.2	GF4978	14.7	14.7	2.48	MC
F434	14.1	GF4990	14.7	14.1	2.47	MC
F435	25.4	GF4998	26.9	26.1	4.11	MC
F436	20.6	GF5004	21.5	21.0	2.78	MC
F437	13.4	GF5007	14.9	14.4	4.98	MC
F438	27.0	GF5034	26.7	27.3	0.98	MC
F439	24.3	GF5052	20.4	20.4	12.14	MC
F440	19.9	GF5054	21.7	20.8	4.02	MC
F546	27.6	GF5775	23.1	23.1	2.58	MC
F547	17.0	GF5787	17.5	17.2	1.00	MC
F548	19.5	GF5797	18.9	18.8	0	MC
F549	24.9	GF5807	22.2	22.5	9.16	MC
F550	14.8	GF5817	15.0	14.9	1.17	MC
F551	15.5	GF5829	16.5	16.0	4.38	MC
F552	24.2	GF5838	13.7	20.9	14.7	MC
F553	17.0	GF5846	15.0	16.0	8.71	MC
F554	14.8	GF5856	17.0	15.9	9.87	MC
F556	24.7	GF5876	22.2	22.9	4.36	MC
F557	16.0	GF5966	14.8	15.4	5.61	MC
F559	18.3	GF5987	19.0	19.2	2.89	MC
F560	11.8	GF5917	11.8	11.3	0	MC
F561	17.3	GF5937	17.3	17.3	0	MC
F562	15.6	GF5935	15.6	15.7	0	MC
F563	22.3	GF5945	22.7	22.2	0	MC
F564	26.1	GF5955	24.9	25.9	2.10	MC
F565	33.7	GF5965	35.1	34.4	2.94	MC
F566	27.3	GF5975	27.3	27.1	0	MC
F567	19.9	GF5985	22.5	21.0	1.71	MC
F568	25.1	GF5995	16.0	20.7	10.9	MC
F569	22.0	GF6005	19.9	20.0	7.21	MC
F570	14.0	GF6015	14.7	14.0	2.50	MC
F571	26.8	GF6025	26.6	26.0	0.6	MC
F572	29.9	GF6034	29.4	29.4	0	MC

# APPENDIX - QUALITY CONTROL

## FEP

## BLOOD

OL. SAMPLE	FE CONC.	LOPP. SAMPLE	FE CONC.	COEFFICIENT OF VARIATION (%)		SMLTP
				MEAN	STANDARD DEVIATION	
F623	31.8	GF6045	33.2	32.5	3.11	FA
F627	16.6	GF6142	17.3	16.9	3.14	SA
F628	20.2	GF6151	21.1	20.2	0.85	SA
F639	14.5	GF6161	13.5	14.0	5.65	SA
F630	26.1	GF6171	28.6	24.3	6.49	SA
F631	20.3	GF6182	18.6	19.4	6.39	SA
F632	20.7	GF6192	19.9	20.1	0.64	SA
F633	24.4	GF6202	24.7	24.6	0.73	SA
F634	22.9	GF6212	22.3	22.6	0.37	SA
F635	20.7	GF6219	19.9	20.3	1.64	SA
F636	22.9	GF6228	22.7	22.8	0.78	PA
F637	15.6	GF6238	15.1	15.2	2.32	PA
F638	23.7	GF6249	23.7	23.7	0	PA
F639	20.9	GF6259	21.3	21.0	0.85	PA
F640	23.7	GF6269	24.4	24.1	2.22	PA
F641	17.9	GF6280	19.7	18.3	2.93	PA
F642	18.4	GF6290	18.7	18.5	0.96	PA
F643	22.2	GF6297	21.4	21.8	0.49	PA
F644	23.4	GF6307	23.7	23.0	0.77	PA
F645	24.0	GF6317	21.7	22.8	2.12	PA
F646	27.8	GF6327	41.6	34.7	6.85	PA
F647	24.8	GF6327	27.5	28.7	5.67	PA
F648	20.4	GF6347	21.7	21.0	4.22	PA
F649	24.0	GF6357	24.0	24.0	0	PA
F650	72.2	GF6367	71.0	71.6	1.11	PA
F651	20.6	GF6374	20.1	20.3	1.12	PA
F652	27.8	GF6384	28.0	27.9	0.67	PA
F653	22.4	GF6394	23.2	22.3	0.75	PA
F654	29.9	GF6405	20.0	29.9	2.59	PA
F655	23.3	GF6417	34.5	30.9	2.57	PA
F656	20.1	GF6427	27.2	28.7	6.63	PA
F657	23.9	GF6435	24.6	24.1	2.13	PA
F658	19.7	GF6445	20.7	20.2	3.45	PA
F659	12.2	GF6454	12.1	12.2	1.22	PA
F660	16.7	GF6463	17.5	17.1	2.65	PA
F661	17.2	GF6477	18.0	17.6	2.97	PA
F667	28.6	GF7032	32.7	31.2	11.3	PA
F690	26.5	GF7043	26.5	26.5	0	PA
F699	17.3	GF7052	18.4	17.8	4.05	PA
F710	101.7	GF7061	71.3	86.4	24.2	PA
F711	20.1	GF7074	25.0	27.1	10.7	PA
F712	17.3	GF7084	16.3	16.7	4.22	PA
F713	55.9	GF7094	54.4	54.1	2.00	PA
F714	19.1	GF7104	20.4	19.4	1.51	PA
F715	25.0	GF7114	26.5	25.9	4.21	PA

APPENDIX - QUALITY CONTROL

FEP  
BLOOD

QC SAMPLE	FP CONC.	COMP. SAMPLE	FP CONC.	MEAN	COEFFICIENT OF VARIATION (%)	SMTP
F716	19.0	GF7132	14.8	14.9	1.21	RP
F717	19.0	GF7132	19.0	19.1	3.74	RG
F718	20.8	GF7142	20.8	22.0	6.04	RG
F719	41.8	GF7152	41.8	42.9	3.09	RG
F720	29.6	GF7162	29.8	29.4	0.60	RG
F721	20.8	GF7172	21.3	22.1	4.93	RG
F722	37.3	GF7182	37.5	38.4	3.39	RG
F723	61.2	GF7192	61.9	62.1	2.62	RG
F724	17.5	GF7202	17.5	18.7	6.04	RG
F725	14.6	GF7212	14.6	17.1	3.05	RG
F726	21.0	GF7222	21.8	21.4	3.67	RG
F727	39.5	GF7230	39.7	39.1	1.96	RG
F728	39.3	GF7240	39.3	39.1	4.89	FL
F729	22.0	GF7250	22.4	21.2	3.11	FL
F730	39.8	GF7260	39.9	39.4	1.94	FL
F731	39.7	GF7270	39.9	39.7	1.96	FL
F732	36.7	GF7281	36.2	35.4	2.82	FL
F733	21.3	GF7291	21.6	21.4	0.89	FL
F734	24.0	GF7301	23.2	23.1	3.42	FL
F735	36.2	GF7312	36.7	36.1	1.58	FL
F736	38.1	GF7322	38.0	38.2	0.50	FL
F737	56.0	GF7332	56.7	56.5	4.52	FL
F738	24.0	GF7342	24.0	24.3	0	FL
F739	33.1	GF7354	33.7	34.1	6.67	RP
F740	52.2	GF7365	50.4	51.1	2.53	RP
F741	20.3	GF7375	20.3	20.1	0	RP
F742	30.9	GF7385	30.5	29.7	1.73	RP
F743	13.1	GF7395	13.1	13.1	0	RP
F744	20.3	GF7402	19.3	19.9	3.71	RP
F745	22.4	GF7412	22.2	21.1	0.81	RP
F746	14.6	GF7422	14.6	14.6	0	RP
F747	22.2	GF7432	21.1	21.6	1.41	RP
F748	42.8	GF7441	41.0	41.1	3.09	RP
F749	28.7	GF7452	28.7	29.1	6.57	RP
F750	20.3	GF7461	20.3	20.2	1.75	RL
F751	32.6	GF7471	32.6	32.1	2.23	RL
F752	22.2	GF7481	22.4	22.2	2.42	RL
F753	39.7	GF7492	39.7	39.7	0	RL

# APPENDIX - QUALITY CONTROL

## LEAD

## BLOOD

ID SAMPLE	PB CONC.	COMP. SAMPLE	PB CONC.	COEFFICIENT OF VARIATION %		SPLIT
				HOME	LAB	
F382	40.1	GF3502	37.3	41.7	14.8	HI
F393	17.7	GF3529	18.3	18.1	2.32	HI
F364	36.5	GF3542	36.4	32.4	12.5	HI
F395	18.6	GF3564	14.2	17.5	19.2	HI
F396	15.1	GF3575	12.8	12.4	11.4	HI
F397	27.9	GF3580	9.07	12.5	72.9	HI
F398	13.1	GF3588	14.1	12.0	5.26	HI
F419	3.51	GF4864	9.77	4.24	64.9	HI
F420	9.89	GF4877	15.5	12.0	35.2	HI
F421	12.2	GF4893	9.22	12.2	15.1	HI
F433	7.26	GF4890	14.3	10.8	46.3	HI
F433	7.92	GF4897	15.7	12.3	50.4	HI
F434	7.04	GF4899	11.9	9.48	35.9	HI
F475	10.6	GF4903	18.1	17.1	37.2	HI
F426	2.87	GF4913	11.8	7.26	65.3	HI
F437	18.3	GF4931	5.32	11.6	27.2	HI
F438	12.5	GF4933	3.13	12.0	16.2	HI
F439	12.5	GF4938	9.36	10.5	12.6	HI
F430	23.3	GF4951	14.0	15.7	15.2	HI
F431	12.3	GF4954	3.96	10.0	21.3	HI
F432	26.1	GF4959	15.2	21.0	34.1	HI
F413	19.6	GF4978	15.0	17.2	16.0	HI
F434	14.0	GF4990	14.1	17.1	0.23	HI
F435	12.8	GF4998	12.9	12.8	0.17	HI
F436	12.3	GF5004	14.9	13.6	13.4	HI
F437	16.0	GF5007	17.4	16.7	2.02	HI
F438	14.4	GF5034	15.1	14.7	1.55	HI
F439	22.0	GF5052	20.2	21.4	4.18	HI
F440	28.2	GF5054	20.1	22.2	24.4	HI
F442	20.5	GF5062	10.6	22.6	44.8	HI
F443	17.3	GF5609	9.25	17.5	26.7	HI
F448	10.6	GF5612	14.5	10.3	15.3	HI
F449	13.5	GF5615	26.4	25.0	24.7	HI
F450	24.9	GF5622	20.5	22.0	2.27	HI
F451	21.4	GF5627	14.0	17.7	13.4	HI
F452	20.2	GF5631	17.2	12.5	11.1	HI
F453	15.5	GF5655	13.2	14.2	10.7	HI
F454	12.1	GF5653	15.0	14.1	0.22	HI
F455	22.2	GF5660	22.0	22.3	2.4	HI
F456	21.0	GF5679	16.2	12.5	19.1	HI
F457	12.1	GF5680	16.2	12.9	3.23	HI
F458	24.2	GF5642	12.2	12.7	3.40	HI
F459	24.0	GF5707	12.6	22.2	3.44	HI
F460	18.2	GF5709	16.7	22.2	1.32	HI
F461	31.7	GF5754	27.4	22.2	42.7	HI



# APPENDIX - QUALITY CONTROL

## LEAD

## BLOOD

QC SAMPLE	FE CONC.	CORR. SAMPLE	FE CONC.	MEAN	COEFFICIENT OF VARIATION %	SD
1462	23.0	GF2762	25.4	24.2	6.90	01
1463	19.3	GF2789	22.6	21.9	11.5	04
1464	17.7	GF2786	22.9	20.1	16.8	08
1465	21.1	GF2787	25.4	22.0	12.9	08
1504	23.2	GF3804	29.2	26.2	16.1	07
1505	16.6	GF3806	33.9	28.0	58.3	01
1506	12.5	GF3816	17.2	14.4	28.0	02
1507	17.6	GF3820	37.9	32.0	23.1	02
1508	23.7	GF3842	55.4	39.6	58.7	01
1509	11.0	GF3846	19.7	16.5	36.2	01
1510	21.3	GF3851	43.2	20.2	47.3	07
1511	16.6	GF3853	27.3	22.1	33.6	07
1512	14.4	GF3870	15.8	15.1	6.81	02
1513	21.7	GF4091	16.0	13.0	21.0	01
1514	6.12	GF4095	6.93	6.10	3.24	01
1515	19.9	GF4099	22.8	21.4	6.43	01
1516	19.1	GF4102	13.1	16.1	23.0	01
1517	17.7	GF4105	8.23	13.4	50.9	01
1518	13.5	GF4108	11.7	12.6	10.2	01
1519	14.1	GF4112	12.5	13.0	6.27	01
1520	19.8	GF4121	19.1	15.4	2.55	01
1521	19.3	GF4156	10.9	15.1	29.3	01
1522	12.1	GF4158	15.0	14.4	19.9	01
1523	5.81	GF4178	9.06	7.44	11.0	01
1524	29.6	GF4189	28.7	25.7	2.30	02
1542	13.9	GF5275	25.0	17.4	41.2	05
1543	7.6	GF5287	13.6	11.4	9.01	06
1546	16.5	GF5297	17.9	17.1	2.81	01
1547	15.1	GF5307	16.4	17.2	1.81	05
1550	24.7	GF5317	23.5	21.0	13.2	05
1551	20.0	GF5328	18.8	13.4	7.55	05
1552	15.7	GF5333	19.3	16.0	2.09	01
1553	14.1	GF5342	13.2	12.7	4.80	01
1554	12.9	GF5356	13.2	13.5	10.1	01
1555	11.9	GF5372	15.3	12.6	17.4	07
1557	9.67	GF5386	9.83	9.25	1.23	04
1559	14.3	GF5397	15.5	12.0	8.01	01
1560	11.4	GF5317	14.0	12.4	18.8	01
1561	12.1	GF5337	12.7	12.4	1.53	01
1562	7.55	GF5335	5.31	6.44	14.5	02
1563	13.1	GF5346	34.1	31.0	1.16	01
1564	20.0	GF5355	32.0	32.3	1.23	01
1565	12.1	GF5360	20.0	17.0	1.81	01
1566	43.2	GF5375	20.3	17.0	1.81	01
1567	20.8	GF5385	13.6	13.7	15.4	01

# APPENDIX - QUALITY CONTROL

## LEAD

## BLOOD

QC SAMPLE	PB CONC.	COMP. SAMPLE	PB CONC.	COEFFICIENT OF VARIATION (%)		
				MEAN	STDEV	SLTP
F568	14.0	GF5995	12.4	13.6	12.3	B0
F569	20.7	GF6005	20.1	20.1	1.87	B0
F570	20.9	GF6015	18.2	19.6	9.65	B0
F571	22.5	GF6025	22.9	23.2	1.90	B0
F572	23.4	GF6034	21.1	22.3	7.56	B0
F573	21.8	GF6045	24.7	23.2	9.77	B0
F578	12.1	GF4195	9.68	11.9	26.2	B0
F579	20.0	GF4201	11.2	15.6	40.1	B0
F580	14.3	GF4206	6.05	10.2	57.3	B0
F581	17.0	GF4219	9.41	12.7	40.5	B0
F582	19.7	GF4231	14.2	17.0	22.0	B0
F583	19.4	GF4241	14.6	17.6	19.9	B0
F584	23.7	GF4247	16.1	19.9	27.0	B0
F617	12.9	GF3986	9.67	11.1	28.5	B0
F618	17.5	GF3997	14.3	15.9	14.5	B0
F619	9.67	GF4007	4.13	6.40	50.1	B0
F620	9.53	GF4017	10.1	9.37	1.45	B0
F621	11.6	GF4027	7.17	9.36	33.1	B0
F622	21.8	GF4033	18.7	20.0	18.3	B0
F623	17.9	GF4046	13.2	13.9	2.96	B0
F624	18.0	GF4050	13.9	16.3	31.0	B0
F625	12.0	GF4066	8.98	10.7	20.6	B0
F626	12.9	GF4070	12.1	12.0	4.23	B0
F627	15.2	GF6142	14.4	14.7	4.67	B0
F628	9.85	GF6151	7.47	8.6	19.5	B0
F629	10.6	GF6161	8.12	9.24	16.4	B0
F630	11.2	GF6171	12.1	12.0	2.51	B0
F631	12.3	GF6182	10.4	11.0	17.2	B0
F632	12.1	GF6193	16.0	15.7	31.1	B0
F633	16.2	GF6202	22.9	17.5	24.4	B0
F634	13.9	GF6212	15.1	14.5	6.17	B0
F635	5.40	GF6218	4.76	5.21	1.61	B0
F636	14.7	GF6223	14.7	14.7	0.23	B0
F637	11.0	GF6236	8.51	10.1	21.1	B0
F638	12.2	GF6246	12.2	12.6	3.34	B0
F639	11.9	GF6259	20.1	17.0	16.0	B0
F640	11.5	GF6269	16.2	17.9	24.3	B0
F641	4.98	GF6280	14.8	10.2	47.1	B0
F642	17.1	GF6280	20.1	17.1	24.7	B0
F643	10.3	GF6297	16.0	17.1	22.6	B0
F644	12.4	GF6307	16.7	16.7	2.27	B0
F645	14.0	GF6317	19.5	17.0	26.1	B0
F646	21.2	GF6327	25.1	24.7	7.97	B0
F647	10.1	GF6337	15.1	15.1	0.0	B0
F648	15.2	GF6347	19.1	17.1	11.4	B0

# APPENDIX - QUALITY CONTROL

## ZINC

## BLOOD

CP SAMPLE	ZN CONC.	COMP. SAMPLE	ZN CONC.	MEAN	COEFFICIENT OF VARIATION %	MULTIPLY
F419	129.	GF4864	375.	374.	53.2	BA
F420	331.	GF4877	343.	344.	21.26	BA
F421	441.	GF4883	369.	405.	12.7	BA
F422	426.	GF4890	564.	495.	19.6	BA
F423	375.	GF4897	422.	394.	8.27	BA
F424	365.	GF4899	330.	341.	7.21	BA
F425	348.	GF4903	180.	283.	45.1	BA
F426	359.	GF4913	431.	391.	8.04	BA
F427	401.	GF4931	430.	449.	12.6	BA
F428	360.	GF4932	377.	373.	1.71	BA
F429	393.	GF4938	476.	371.	32.5	BA
F430	419.	GF4931	422.	421.	2.14	BA
F431	384.	GF4954	313.	454.	6.73	BA
F432	131.	GF4963	255.	213.	24.1	BA
F433	410.	GF4978	462.	421.	8.45	BA
F434	353.	GF4990	329.	341.	4.98	BA
F435	374.	GF4993	367.	377.	1.69	BA
F436	382.	GF5004	444.	417.	10.1	BA
F437	452.	GF5007	436.	463.	5.22	BA
F438	424.	GF5024	436.	410.	2.64	BA
F439	384.	GF5052	326.	321.	7.62	BA
F440	444.	GF5054	371.	397.	12.7	BA
F441	407.	GF2603	163.	215.	8.01	BA
F442	464.	GF2639	474.	461.	1.39	BA
F443	405.	GF2613	374.	367.	5.62	BA
F444	401.	GF2615	438.	473.	4.37	BA
F445	331.	GF2633	384.	313.	13.3	BA
F446	336.	GF2627	144.	244.	2.57	BA
F447	506.	GF2631	127.	452.	40.1	BA
F448	477.	GF2655	139.	411.	12.7	BA
F449	438.	GF2656	430.	432.	3.00	BA
F450	413.	GF2660	324.	367.	17.0	BA
F451	383.	GF2679	316.	336.	12.6	BA
F452	408.	GF2682	340.	371.	12.8	BA
F453	427.	GF2699	373.	407.	8.45	BA
F454	508.	GF2707	442.	416.	4.39	BA
F455	531.	GF2729	451.	451.	11.5	BA
F456	575.	GF2754	551.	510.	2.51	BA
F457	542.	GF2763	537.	511.	5.80	BA
F458	580.	GF2760	557.	513.	9.75	BA
F459	430.	GF2766	477.	451.	5.61	BA
F460	517.	GF2767	343.	371.	2.35	BA
F461	512.	GF2804	366.	371.	14.1	BA
F462	507.	GF2866	327.	371.	3.31	BA
F463	510.	GF2812	312.	371.	2.97	BA

# APPENDIX - QUALITY CONTROL

## LEAD

## BLOOD

QC SAMPLE	PB CONC.	CORR. SAMPLE	PB CONC.	COEFFICIENT OF		SULTP
				MEAN	VARIATION, %	
1782	14.1	GF7354	22.0	18.7	31.1	AD
1783	17.5	GF7365	27.3	22.4	31.0	AD
1784	6.02	GF7375	15.3	11.7	44.1	AD
1785	23.1	GF7385	26.7	24.4	18.1	AD
1786	14.0	GF7395	19.2	16.6	22.5	AD
1787	9.61	GF7406	18.5	14.1	43.2	AD
1788	10.1	GF7416	19.4	15.6	42.5	AD
1789	15.5	GF7426	18.0	16.7	11.4	AD
1790	13.3	GF7436	17.1	15.1	10.2	AD
1791	18.2	GF7441	22.0	20.1	12.7	AD
1792	10.4	GF7452	20.1	15.5	44.7	HL
1793	2.93	GF7461	8.79	5.60	75.5	HL
1794	10.8	GF7471	12.1	11.4	5.52	HL
1795	14.4	GF7483	17.5	15.7	11.3	HL
1796	17.1	GF7492	19.9	19.5	12.2	HL

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# APPENDIX - QUALITY CONTROL

## LEAD

## BLOOD

ID	SAMPLE	PB CONC.	COMP. SAMPLE	PB CONC.	MEAN	COEFFICIENT OF VARIATION, %		SD
						1.0	1.0	
1649	12.1		GF6357	12.0	12.1	0.57		AL
1650	16.3		GF6367	16.1	16.2	0.85		AL
1651	17.8		GF6374	20.7	19.2	10.8		AL
1652	17.2		GF6384	11.5	14.3	29.1		AL
1653	16.0		GF6394	10.6	12.1	28.3		AL
1654	24.2		GF6405	23.7	24.0	1.55		AL
1655	14.7		GF6417	13.7	14.2	4.87		AL
1656	14.7		GF6437	14.3	14.5	1.30		AL
1657	14.3		GF6438	12.0	12.4	10.0		AL
1658	17.8		GF6445	15.8	17.6	17.1		AL
1659	7.28		GF6454	17.2	11.4	55.0		AL
1660	12.4		GF6462	13.2	12.8	3.30		AL
1661	15.3		GF6467	18.8	17.0	24.1		AL
1707	21.9		GF7032	18.4	20.2	10.4		AL
1708	11.6		GF7043	11.5	11.5	0.53		AL
1709	10.7		GF7053	17.6	14.2	34.4		AL
1710	17.6		GF7063	26.5	22.1	29.7		AL
1711	13.8		GF7074	20.1	17.2	18.1		AL
1712	18.4		GF7084	37.9	22.1	38.9		AL
1713	24.1		GF7094	33.0	29.1	92.0		AL
1714	16.4		GF7104	30.4	29.4	69.3		AL
1715	6.44		GF7114	2.89	7.69	11.2		AL
1716	8.97		GF7123	12.5	10.7	23.6		AL
1717	10.5		GF7132	19.6	17.4	42.6		AL
1718	12.3		GF7142	13.8	11.0	7.86		AL
1719	18.5		GF7152	19.2	14.2	2.64		AL
1720	4.11		GF7162	14.2	5.17	78.0		AL
1721	8.00		GF7172	12.5	6.07	124.1		AL
1722	17.2		GF7182	21.0	15.1	14.1		AL
1723	9.46		GF7192	10.1	9.17	4.15		AL
1724	17.3		GF7202	23.5	20.6	19.4		AL
1725	0.82		GF7212	10.4	10.1	1.78		AL
1726	11.9		GF7222	17.2	14.6	26.7		AL
1727	13.7		GF7232	13.3	21.0	16.2		AL
1728	6.24		GF7240	10.2	21.5	34.4		AL
1729	12.2		GF7250	16.1	14.1	13.7		AL
1730	12.7		GF7260	21.4	17.1	18.7		AL
1731	5.27		GF7270	12.4	5.00	23.6		AL
1732	9.03		GF7281	17.2	12.1	12.2		AL
1733	8.90		GF7291	13.3	12.2	22.7		AL
1734	16.9		GF7301	21.1	17.1	15.6		AL
1735	19.7		GF7312	13.6	16.7	21.5		AL
1736	0.00		GF7322	11.2	7.0	11.7		AL
1737	6.95		GF7332	12.1	13.1	12.2		AL
1738	9.18		GF7342	11.1	8.07	12.1		AL

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